Structure and Functionality of an Alkylated Li$_x$Si$_y$O$_z$ Interphase for High-Energy Cathodes from DNP-ssNMR Spectroscopy

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ABSTRACT: Degradation processes at the cathode−electrolyte interface are a major limitation in the development of high-energy lithium-ion rechargeable batteries. Deposition of protective thin coating layers on the surface of high-energy cathodes is a promising approach to control interfacial reactions. However, rational design of effective protection layers is limited by the scarcity of analytical tools that can probe thin, disordered, and heterogeneous phases. Here we propose a new structural approach based on solid-state nuclear magnetic resonance spectroscopy coupled with dynamic nuclear polarization (DNP) for characterizing thin coating layers. We demonstrate the approach on an efficient alkylated Li$_x$Si$_y$O$_z$ coating layer. By utilizing different sources for DNP, exogenous from nitroxide biradicals and endogenous from paramagnetic metal ion dopants, we reveal the outer and inner surface layers of the deposited artificial interphase and construct a structural model for the coating. In addition, lithium isotope exchange experiments provide direct evidence for the function of the surface layer, shedding light on its role in the enhanced rate performance of coated cathodes. The presented methodology and results advance us in identifying the key properties of effective coatings and may enable rational design of protective and ion-conducting surface layers.

1. INTRODUCTION

The electrode−electrolyte interface plays a crucial role in the electrochemical performance of rechargeable batteries and in particular in lithium-ion battery (LIB) cells.1,2 Chemical and electrochemical reactions at the interface result in deposition of interphases which modify interfacial properties, such as electronic and ionic conductivity, and can thus completely block access to the electrode material. These reactions and their products have been thoroughly investigated on the anode side in LIBs, and great efforts were invested in identifying favorable conditions for the formation of a solid electrolyte interphase (SEI): interphases that will block electron transport and will prevent further reactivity with the electrolyte while still enabling efficient ion transport across the SEI.2−4 The cathode interface, on the other hand, which was initially thought to lead to negligible electrolyte decomposition, currently poses one of the key challenges in the development of high-energy LIB cells. This is due to the plethora of interfacial processes identified on the surface of high-energy cathodes, including electrolyte oxidation, metal ion dissolution, structural transformations, and oxygen evolution.5,6 Therefore, achieving control over cathode interfacial reactivity is essential for the development of high-energy cells.

A leading approach for gaining such control is through deposition of an artificial cathode−electrolyte interphase (CEI).7,8 Such CEI layers act as a passivating barrier between the cathode and the electrolyte and ideally should prevent chemical and structural degradation while maintaining ionic permeability. Despite the significant progress made in synthetic approaches to form highly efficient CEIs, far less is known about what are the properties that make a beneficial CEI. The ability to rationally design a permeable and passivating CEI is limited by the scarcity of analytical tools that can be used to probe thin (few nanometers), disordered, and heterogeneous layers. Furthermore, the ion transport properties of such interphases are mostly inferred from electrochemical impedance spectroscopy (EIS)9−11 and recently also modeling,12−15 and not from direct measurements of these phases. In recent years, the use of solid-state NMR (ssNMR) spectroscopy to characterize battery materials has increased considerably.16,17 The main advantage of this approach is its high chemical specificity, which combined with its short-range structural sensitivity, can be used to determine the chemical composition,
of the CEI. We combine the exogenous DNP approach, where 
interfaces,23 including the SEI and interphases formed on 
increase in sensitivity. Such a boost in sensitivity enables the 
exchange process of the two NMR-active isotopes of lithium, 
6,7Li. By tracking the exchange process, we gain direct insight 
into the functionality of the CEI and its role in ion transport 
across the electrode—electrolyte interface.

2. MATERIALS AND METHODS

2.1. Materials. The synthesis of spherical TiO2 particles followed 
the previously reported procedure.36 Fe-doped TiO2 (Fe−TiO2) particles were synthesized in two 
consecutive steps: (i) synthesis of amorphous spherical Fe doped 
titanium glycolate through precipitation and (ii) high-temperature 
annealing/calcination of the resulting Fe−TiO2.37 For the first step, 
50 mL of ethylene glycol (EG, Sigma-Aldrich) was put in a 100 mL 
conical flask and purged with nitrogen for 30 min under continuous 
stirring to remove dissolved oxygen. Next, 4.725 mg (0.5 mol %) of 
Fe(NO3)3·9H2O (Sigma-Aldrich) was added to the EG solution 
followed by the dropwise addition of 0.8 mL of tetrabutoxytitanium 
(Sigma-Aldrich). After 15 min of stirring, the resulting solution was 
sealed with parafilm and stirred for another 8−10 h at room 
temperature. The obtained transparent mixture was then added into 
200 mL of acetone, followed by addition of 2 mL of water. The 
mixture was then sealed with parafilm and stirred for another 1−2 h. 
The white precipitate obtained, composed of spherical Fe-doped 
titanium glycolate, was collected by centrifugation, washed with 
ethanol three times, and dried overnight at 60 °C. Further annealing 
of the powder at 350 °C for 3 h, ramp rate of 1 °C/min, led to 
spherical Fe−TiO2 particles.

Li2SiO3 molecular layer deposition (MLD) treatment of TiO2, 
Fe−TiO2, and LMR-NMC particles was identical with the previously 
reported procedure.36

2.2. Characterization Techniques. The crystal structure and 
purity of lithium metasilicate were determined by powder X-ray
were then washed three times with anhydrous DMC to remove residual electrolyte and dried overnight in the glovebox precharger. The electrolyte for these experiments was prepared by dissolving the appropriate amount of $^6\text{LiPF}_6$ (Sigma-Aldrich) in 1:1 weight ratio of EC (Alfa Aesar) and DMC (Sigma-Aldrich).

### 2.5. ssNMR Experiments

Solid-state NMR experiments were performed on a Bruker 9.4 T Bruker Avance III and Avance Neo 400 MHz wide bore spectrometers. Samples were packed into rotors with an outer diameter of 1.3 or 4 mm for magic-angle spinning experiments with sample spinning at 50 and 10 kHz, respectively. Details on specific samples and experimental parameters used are given in Tables S1–S4. $^7\text{Li}$ spectra were referenced to LiF at ~1 ppm, and $^6\text{Li}$ experiments were referenced to Ni-doped lithium titanate at 0 ppm. Quantification of spectra was done with the TOPSPIN program.

### 2.6. Magic-Angle Spinning DNP Experiments

DNP experiments were performed on a Bruker 9.4 T Avance Neo spectrometer equipped with a sweep coil and a 263 GHz gyrotron system. We used 3.2 mm triple and double resonance low-temperature DNP probes for the experiments at magic-angle spinning of 10 kHz. All experiments were performed at about 100 K, with sample temperature of about 99 and 105 K without and with microwave irradiation, respectively. All spectra were acquired after the sample temperature was stable. Longitudinal relaxation, $T_1$, and polarization buildup time were used for selection of magic-angle spinning experiments.

### 3. RESULTS AND DISCUSSION

#### 3.1. CEI Composition and Structure

Characterization of the coating was first attempted on the Li$_3$Si$_2$O$_7$-coated LMR-NMC powder. Detection of $^7\text{Li}$ environments in the coating proved challenging due to significant spectral overlap with the dominant lithium resonances from the bulk of the cathode (Figure S1). To avoid interference from the bulk, experiments were performed on Li$_3$Si$_2$O$_7$-coated TiO$_2$. Room temperature $^7\text{Li}$ MAS experiments resulted in a poor signal-to-noise ratio in $^7\text{Li}$ spectra, even after 24 h of acquisition from ~100 mg sample (Figure S2). Cross-polarization experiments are commonly used to increase the sensitivity of low abundance and/or low sensitivity nuclei by transferring the polarization from $^7\text{Li}$ nuclei with large magnetic moment and high abundance to nuclei in close proximity (a few angstroms). However, the limited thickness of the coating also prevented
detection of $^{29}$Si resonance through $^1$H–$^{29}$Si cross-polarization experiments. Thus, to gain sensitivity in probing the coating without interference from bulk signals, the coating was further characterized through magic-angle spinning DNP measurements on the Li$_2$Si$_2$O$_5$-coated TiO$_2$ samples. Two DNP approaches were used, differing in the location of the polarization source (schematically described in Figure 1), to provide sensitivity to different areas of the coating.

3.1.1. Exogenous DNP. Exogenous DNP experiments were performed on coated TiO$_2$ particles by wetting the sample with 16 mM TEKPol in tetrachloroethane solution following the common approach for DNP surface-enhanced NMR spectroscopy. The polarization of the $^1$H of tetrachloroethane, with 250-fold enhancement from DNP (Figure 2a), was transferred to the $^{29}$Si, $^{13}$C, and $^7$Li species in the lithium silicate thin surface layer through cross-polarization, enabling the assignment of the local environments in the CEI. In the $^1$H–$^{29}$Si cross-polarization spectrum (Figure 2b), four $^{29}$Si environments were detected and assigned: double and monoalkylated silica groups resonating at $-20$ and $-60$ ppm, respectively, an amorphous silica environment at $-110$ ppm, and a triple alkylated silicon group at $17$ ppm (R$-coated TiO$_2$ samples. Two DNP approaches were used, differing in the location of the polarization source (schematically described in Figure 1), to provide sensitivity to different areas of the coating.

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Indirect DNP from $^1$H nuclei to $^{13}$C nuclei, shown in Figure 2c, revealed four carbon groups that are assigned to the tert-butyl environment (20, 27, and 37 ppm) and methyl groups (1.85 ppm) originating from the single source MLD precursor material. A broad $^7$Li resonance, centered at 0 ppm, was identified through polarization transfer from $^1$H nuclei (Figure 2d), suggesting that lithium sites are accessible to the solvent and are found on the outer surface layer of the lithium silicate coating. Table 1 summarizes the various environments found in the lithium silicate coating layer, with their chemical shifts.

To determine whether the detected Li and Si environments are found in the same phase in the thin coating layer, distance measurement experiments were performed with the $^1$H–$^{29}$Si-

### Table 1. Lithium Silicate Compositional Environments and Chemical Shift Assignments

| nucleus | chemical shift (ppm) | assignment | ref |
|---------|---------------------|------------|-----|
| $^1$H   | 6.4                 | tetrachloroethane |   |
| $^{29}$Si | 17                | R$_1$Si(OR)$_2$ | 40, 42 |
|         | $-20$               | R$_2$Si(OR)$_3$ | 40  |
|         | $-60$               | R-Si(OR)$_3$  | 40  |
|         | $-110$              | SiO$_2$     | 41  |
| $^{13}$C | 20, 27, and 37     | (CH$_3$)$_2$CH- | 42, 43 |
|         | 1.85                | CH$_3$      | 42, 43 |
| $^7$Li  | 0                   | interfacial lithium | 44  |

(R is assigned to an alkyl group. R$'$ is assigned to $^1$H or an alkyl group.

$^7$Li cross-polarization rotational echo double resonance (cross-polarization REDOR, Figure 3a) technique, enabled by the sensitivity gained from DNP. This technique reintroduces the dipolar coupling between the lithium and silicon nuclei, which are otherwise averaged out by magic-angle spinning. Measurements of the signal decay with increased dipolar recoupling time provide information about the proximity between Si and Li environments. To account for the decay due to $^{29}$Si transverse relaxation, the signal with recoupling pulses on the $^7$Li (S) is divided by the reference signal without recoupling pulses ($S_0$). In Figure 3b, the S and $S_0$ spectra, acquired following a dephasing period of 3 ms, are compared for the lithium silicate-coated TiO$_2$, showing that there is no significant difference between the spectra (above the noise level). These results were compared with the $^7$Li–$^{29}$Si($^7$Li) cross-polarization REDOR experiment performed on a model compound, lithium metasilicate, having close Si and Li pairs within $3\text{ Å}$ (Figure S3a). The resonance of the main $^{29}$Si environment in the lithium metasilicate, at $-75$ ppm (resonances at $-65$ and $-100$ ppm are assigned to Li$_2$SiO$_4$ and SiO$_2$ impurities, respectively), completely decayed in $<1$ ms recoupling time (Figure 3c).

In Figure 3d, the dephasing curves for the Li$_2$Si$_2$O$_5$–TiO$_2$ and the model compound are compared. Numerical simulations performed with SPINEVOLUTION (see Figure S3b) suggest that the Li–Si pairs in the coating have to be more than 6 Å apart; otherwise, they would show measurable decay. Thus, we can conclude from these REDOR experiments that the direct bonds between Li and Si atoms in the precursor.
dissociate during the MLD process, leading to Li sites being at least 6 Å removed from Si sites, most likely in separate phases.

The DNP surface-enhanced NMR spectroscopy approach provides excellent sensitivity to the surface of the sample. The extent of polarization transfer across the surface and toward the bulk typically depends on the ability of the nuclei involved to propagate the polarization through efficient spin diffusion. In the present case, we employed indirect polarization through cross-polarization from 1H nuclei. Thus, we can enhance resonances (of 29Si, 13C, and 7Li) that are directly accessible to the solvent or have proton environments in close proximity (which can get polarized by spin diffusion from the polarized solvent or directly from the nitroxide radicals). Based on this, the precursor used, and the nature of the MLD process, the alkylated species are found at the outer interface of the coating.

**Figure 3.** (a) Pulse sequence for rotational echo double resonance (REDOR) experiment. (b) 1H−29Si{7Li} cross-polarization REDOR DNP experiment performed on the lithium silicate-coated TiO2 sample with polarization time of 5 s, 8800 scans, 2 ms contact time, and 3 ms recoupling time. (c) 7Li−29Si{7Li} cross-polarization REDOR slices acquired from lithium metasilicate with relaxation delay of 90 s, 48 scans, 4 ms contact time, and 2 ms recoupling time. (d) Normalized integrated intensity of 1H/Li−29Si{7Li} cross-polarization REDOR experiments as a function of the recoupling time for lithium silicate-coated TiO2 (green) and for lithium metasilicate for peak at −75 ppm (dark red). Experiments were performed at 100 K with 10 kHz spinning speed.

**Figure 4.** (a–f) HAADF-STEM analysis of Li5Si3O9-coated Fe-TiO2 particles showing the elemental distribution of (c) Ti, (d) O, (e) Fe, and (f) Si. (g) Field sweep echo detected Q-band of Fe−TiO2 (black) and fitted simulation (green) calculated with S = 5/2, g = 1.99, D = 1500 MHz, and E = 0. (h) DNP sweep profile acquired for 7Li direct polarization with a buildup time of 20 s and 4 scans for the lithium silicate-coated Fe-TiO2 sample. The field was set to 9.395 T (blue arrow).

3.1.2. *Endogenous DNP.* To assess the uniformity of the lithium ions distribution throughout the coating layer, as well as obtain insight into the composition of the interface of the coating with the substrate, we employed the endogenous DNP approach. To this end, micrometer-sized TiO2 particles were doped with Fe(III) at a nominal concentration of 0.5% mol (60 mM) (XRD of the synthesized anatase phase is shown in Figure S5) and coated with the Li5Si3O9 surface layer. Figure 4a shows the high-angle annular dark-field images collected in the scanning transmission electron microscope (HAADF-STEM) from the Fe−TiO2-coated powder. The HAADF-STEM analysis (shown in Figure 4b–f) confirmed the homogeneous distribution of the doped iron (atomic fraction of 0.6% ± 0.14%) and the coated silicon (atomic fraction of 0.49% ± 0.13%) (Figures 4e and 4f, respectively). Figure 4g
Figure 5. Top spectra: direct polarization via endogenous DNP from the unpaired electrons of the iron dopant (inset: polarization source represented as red ellipse) to (a) $^7$Li nuclei, acquired with polarization time of 33 s and 128 scans and (c) $^{29}$Si nuclei using CPMG detection, acquired with polarization time of 300 s and 126 scans. Bottom spectra: direct polarization via exogenous DNP from the unpaired electrons of the nitroxide solution (inset) to the (b) $^7$Li nuclei, acquired with polarization time of 100 s and 8 scans and (d) $^{29}$Si nuclei by using CPMG detection, acquired with polarization time of 120 s and 192 scans. Experiments were performed at 100 K with 10 kHz spinning speed. Monoalkylated silica and silica groups are marked with light green and dark green dotted lines, respectively. (e) A structural model of the Li$_4$Si$_2$O$_8$ coating layer showing the various silicon environments in different shades of green. Uniformly distributed LiO$_x$ is shown in blue.

displays the field sweep echo detected EPR spectrum for Fe–TiO$_2$, acquired at 34.2 GHz (Q-band) at 50 K. The spectrum displayed a typical powder pattern of high spin electron species and was fitted with EASYSPIN$^{50}$ to a single site with $S = 5/2$ broadened by zero field splitting with $D$ of 1500 MHz and a similar $D$ strain. A similar pattern was observed for Fe(III) doped in Li$_4$Ti$_5$O$_12$ anode,$^{33}$ further confirming the incorporation of the Fe(III) dopants in the TiO$_2$ particles.

The coated Fe–TiO$_2$ particles were then studied with magic-angle spinning DNP at 100 K. First, a DNP sweep profile was acquired (Figure 4h) by measuring the signal intensity of $^7$Li resonance in the coating (with microwave irradiation) as a function of the magnetic field. The field dependence displayed the typical positive and negative signal enhancement lobes, separated by about twice the Larmor frequency of $^7$Li, suggesting that the DNP mechanism for polarization transfer is the solid effect.$^{51}$ The magnetic field was then set to the position that gave the highest signal intensity (marked by a blue arrow in Figure 4h).

At the optimal magnetic field for polarizing $^7$Li from the iron dopant, with microwave irradiation, the polarization is transferred from the Fe(III) d electrons to the surrounding coupled nuclei. This enabled examination of the environments in the surface layer through direct polarization transfer to $^7$Li and $^{29}$Si as shown in Figures 5a and 5c, respectively. At the optimal position, a polarization buildup time of 23 s was measured for $^7$Li and an enhancement factor of 8 was obtained for the lithium nuclei, at steady state. We note that the enhancement can probably be increased by optimizing the Fe(III) content. $^{29}$Si detection was also enabled by polarization transfer from Fe(III) (without optimization of the field, which would probably result in higher sensitivity) by using CPMG detection with a polarization time of 300 s. Two silicon environments were detected in the CPMG measurements which can be assigned to monoalkylated silica and SiO$_x$ groups (resonating at $-60$ and $-110$ ppm).

Recently, we have shown that direct polarization transfer in the bulk of Fe(III)-doped Li$_4$Ti$_5$O$_12$ is distance independent in cases where the dominant nuclear relaxation mechanism is the paramagnetic dopant.$^{33}$ In the current system, because of the presence of strong dipole moments of $^1$H and $^7$Li in the coating and overall heterogeneity and disorder in the coating layer, it is unlikely that the Fe(III) dopants in the bulk are the only source of relaxation. Thus, we assume direct polarization to be limited in this case to a few atomic layers from the doped TiO$_2$ surface. The fact that lithium and silicon nuclei could be detected by endogenous DNP indicates that there are lithium and silicon environments at the inner surface layer of the coating.

By comparing the resonances detected when polarization is transferred directly from exogenous nitroxide radicals to those detected when polarization is transferred endogenously from the Fe(III) dopants, we can gain structural insight into the arrangement of the phases on the surface. Figures 5b and 5d show the direct polarization of $^7$Li and $^{29}$Si environments, respectively, acquired via polarization transfer from the nitroxide solution to the coupled nuclei. Comparison of the spectra collected with endogenous DNP (upper Figures 5a and 5c) and with exogenous DNP (lower Figures 5b and 5d) suggests that (i) lithium ions are distributed uniformly throughout the coating layer as they can be detected using both polarization sources and (ii) monoalkylated silicon and SiO$_x$ groups are at the inner layer closer to the TiO$_2$ as they are revealed with endogenous DNP and are less exposed to the nitroxide solution, resulting in relatively low intensity with exogenous DNP. We note the comparison is between the chemical environments detected and not the relative intensities in the spectra since different samples and sources for
polarization were employed. Nonetheless, as both sets of experiments were performed by direct polarization which requires the nuclei to be close to the polarization source, they provide structural information about the coating layer.

On the basis of these multinuclear exogenous and endogenous DNP-NMR results, we propose a structural model for the coating layer shown in Figure 5e. The CEI is composed of a thin, open interface of amorphous silica, terminated with siloxanes and alkylated (tert-butyl and methyl) silicon groups. Lithium forms separate domains from the silicon that are uniformly dispersed throughout the coating layer.

### 3.2. Li Ion Mobility across the CEI

We now turn to determine the functionality of the artificial CEI and its role in lithium ion transport across the electrode interface. Previously, we observed improved electrochemical performance, in particular rate performance, for Li$_4$SiO$_2$-coated LMR-NMC compared to the uncoated cathode.\(^{36}\) As galvanostatic cycling tests are performed at the cell level, it is difficult to isolate specific factors leading to the improved performance. EIS measurements were performed to determine the effect of the coating layer on interfacial transport properties. Figure 6 portrays the EIS Nyquist plot measured for the uncoated and coated cathodes following five galvanostatic cycles vs Li metal (Figure S6). Because these measurements were performed in a two-electrode cell, it is not possible to assign the various features in the EIS spectra to one of the electrodes; therefore, only a qualitative discussion can be done, comparing the different electrochemical cells. The spectra show that the semicircle in the high–medium frequency (which can be attributed to charge transfer and surface film resistances\(^{52,53}\)) of the lithium silicate-coated sample is smaller than that of the uncoated sample. This suggests that Li ion migration through the electrode interface is improved with the lithium silicate surface treatment. We cannot rule out the possibility that the higher resistance of the uncoated cathode is a result of CEI formation. CEI formation on LMR-NMC occurs upon cathode soaking in the electrolyte, and an ~12 nm thick CEI has been previously reported following the first discharge.\(^{54,55}\) Nonetheless, the lithium silicate-coated cathode shows lower interfacial impedance.

### 3.2.1. Lithium Isotope Exchange Experiments on LMR-NMC

Isotope exchange experiments were performed to gain direct insight into ion exchange processes across the CEI. Here we made use of the possibility to detect the two NMR-active lithium isotopes: $^6$Li (7.6% natural abundance) and $^7$Li (92.4% abundance). By following the changes in the amount of one of the isotopes, when two lithium-containing phases varying in their isotope ratios are in contact, we can get insight into ionic mobility. A similar approach has been used for quantification of spontaneous diffusion in the electrode bulk\(^{56,57}\) and across the electrode–electrolyte interface.\(^{55,59}\) For isotope enrichment, the uncoated LMR-NMC and lithium silicate-coated LMR-NMC were first cycled vs $^6$Li metal for five cycles, with voltage range of 2.0–4.7 V for the first cycle with a C-rate of C/15 and consecutive cycles with the voltage range 2.0–4.6 V and a C-rate of C/10 (representative electrochemistry profiles shown in Figure 7 and Figure S7). The cathodes were then extracted from the cell, rinsed thoroughly with DMC, and immersed in LP30 (natural isotopes abundance). The $^6$Li content in the cathodes, following different immersion times, was determined by $^6$Li magic-angle spinning NMR. Figures 7a and 8b present the $^6$Li spectra of the uncoated and coated LMR-NMC samples at various immersion times. The percentage of isotope exchange was calculated with respect to the initial state (no immersion) and is plotted in Figure 8c (integrated intensity, normalized by sample weight and number of scans, as a function of time is shown in Figure S8). The initial amount of $^6$Li in the uncoated cathode and the Li$_4$SiO$_2$-coated cathode was similar, yet the slope was significantly different. In the uncoated LMR-NMC a gradual decline in $^6$Li content was observed, reaching 10% decrease after 80 h immersion. A much more pronounced decay was observed for the coated cathode, reaching 55% of its initial $^6$Li content at 80 h.

These results provide direct evidence for improved ion exchange across the artificial CEI and through the bulk of the cathode achieved due to the coating. Because the LMR-NMC particles are 5–10 μm in size,\(^{36}\) it is unlikely that they differ in their bulk properties due to the surface treatment. Thus, we suspect the difference in ion exchange is due to increased interfacial transport achieved by coating the particles. Such improvements can be due to suppression of degradation processes, such as prevention of cracks or CEI formation and/or chemical and structural rearrangement. The CEI formed on

![Figure 6. EIS Nyquist plots measured at the discharged state of the uncoated and lithium silicate coated LMR-NMC electrodes vs Li metal after five cycles.](https://doi.org/10.1021/jacs.1c00215)

![Figure 7. Voltage vs capacity plots for (a) the uncoated LMR-NMC and (b) Li$_4$SiO$_2$-LMR-NMC cycled vs $^6$Li metal. Representative profiles are shown for the 1st cycle and 5th cycle.](https://doi.org/10.1021/jacs.1c00215)
the uncoated LMR-NMC cathode may be the reason for the inferior Li ion dynamics.

3.2.2. Lithium Isotope Exchange Experiments on Coated TiO2. To determine whether the Li3SiO4 surface layer plays an active role in the improved rate performance, beyond acting as a physical barrier, we performed additional isotope exchange experiments on the coated TiO2 particles. Li3SiO4−TiO2 samples were immersed in 0.025 M LiPF6 solution and in a control solution of 0.025 M LiPF6 (at natural abundance) and examined with exogenous DNP. The tetrachloroethane 1H echo spectra (Figure 5a,b) acquired with and without microwave irradiation showed high polarization and high enhancement factors for both samples. Cross-polarization of this solvent enhanced signal enabled detection of the 6Li environments in the coating (Figure 9). The 6Li signals were normalized by the 1H polarization enhancement factor for each sample to remove any differences due to sample preparation which may lead to different enhancements (after taking into account the weight of the sample, number of scans, and receiver gain). Results from direct polarization of 6Li in the coating are shown in Figure S10. In both direct and indirect polarization experiments, the 6Li resonance from the coating was significantly larger after immersion in 6LiPF6 solution compared to the control experiment. This increase is a result of 6Li exchange between the lithium ions in the enriched electrolyte solution and in the lithium silicate surface layer on the TiO2 sample. 29Si spectra (Figure S11), acquired with indirect polarization and CPMG detection, were identical with spectra acquired for samples with no immersion, confirming that the coating layer stayed intact following the immersion in LiPF6 solution.

Thus, we conclude that lithium sites in the Li3SiO4 surface layer are exchangeable, strongly suggesting that the coating layer takes part in the transport process between the electrolyte and the cathode. This functionality of the coating layer leads to efficient lithium transport across the CEI, which along with the mechanical and chemical stability it provides to the cathode results in reduced interfacial resistance and enhanced capacity and rate performance.

4. CONCLUSIONS

In this work, we demonstrated how ssNMR with increased sensitivity from DNP can be used as an excellent probe for thin protection layers used as artificial CEIs of high-energy cathodes. The remarkable sensitivity gained from exogenous DNP enabled multinuclear characterization of the chemical environments formed with a new MLD coating process based on the alkylated silyllithium precursor. REDOR experiments, possible through DNP, revealed separation between lithium and silicon environments. Endogenous DNP was employed for the first time extending the polarization from bulk to surface. Importantly, the combination of these two DNP approaches, polarizing the outer surface layers with exogenous DNP and inner layers with endogenous DNP, proved to be a powerful structural tool. Insight into the three-dimensional architecture of the surface layers suggests that lithium is distributed across the coating layer in a stacked structure, with monolayered silica and SiO2 groups on the interface of the coating with the electrode and organic moieties facing the interface with the electrolyte.

Furthermore, ssNMR proved to be a valuable tool for directly following ionic mobility, a key parameter for the assessment of the functionality of electrode–electrolyte interfaces. Lithium isotope exchange experiments revealed the enhanced ion transport properties of the coated LMR-NMC samples. Additionally, with sensitivity gained from exogenous DNP we were able to show that the lithium sites in the lithium silicate surface layer are exchangeable, providing direct evidence for the role of the coating in the ion transport process. These results provide atomic-scale rationalization of the EIS measurements and the enhanced rate performance observed for coated cathodes, further establishing the coating’s functionality as an efficient protective surface layer for high-energy cathodes.
We expect the presented ssNMR-DNP methodology will be beneficial in the study of other thin, disordered, and heterogeneous surface layers: for rationally designing artificial CEIs and SEIs as well as for understanding the structure and function of electrochemically and chemically formed interphases in battery cells. The ability to correlate the chemical composition, structure, and transport properties of interfaces and interphases is an essential step for developing high-energy, long-lasting energy storage systems. Thus, the presented methodology forms a promising addition to the characterization toolbox of energy storage materials.

**ASSOCIATED CONTENT**

* Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c00215.

Additional NMR and DNP experiments and information: room temperature MAS NMR measurements, experimental details of NMR and DNP experiments, representation of DNP approaches, sample preparation for DNP experiment, crystallographic structure of lithium metasilicate and numerical simulations of 29Si-¹Li REDOR curves; powder XRD of synthesized Fe-doped TiO₂, electrochemical cycling data for LMR-NMC and coated LMR-NMC vs ⁴Li and quantification of NMR signal intensity vs immersion time for lithium isotope exchange experiments, electrochemical cycling data for batteries tested with EIS (PDF). 

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Notes
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