Supporting Information

S1. Potential plateau

We believe that the variation in the potential plateau (between cells operating at similar lithiation rates) up to 20 mV appeared as shown in Fig. 2 most likely originates from the variation of the cell impedance during a long lithiation period. However, the potential plateau profile is very flat (Fig. S1) within such a short time scale as expected for a two-phase system.[16]

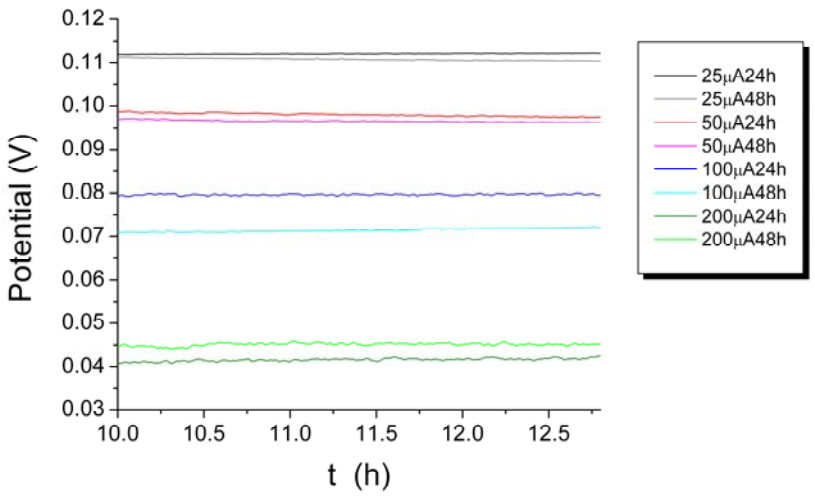

Figure S1. *Potential profile in a short time scale of 2.8 h (~10000 s)*

S2. Independence of the chemical shift on crystal orientation of Si substrate

We confirmed that the angular dependence of chemical shift $\delta(\theta_n)$ is not affected by

the configuration between the external magnetic field and the crystal orientation of Si substrate. The Si wafer was lithiated at a constant current density of 200 μA/cm^2 for 24 hours and $\delta(\theta_n)$ was investigated while rotating the sample along the <100> and <110> direction of the Si substrate. The two curves of $\delta(\theta_n)$ with different rotation axes well coincide as shown in Fig. S2.

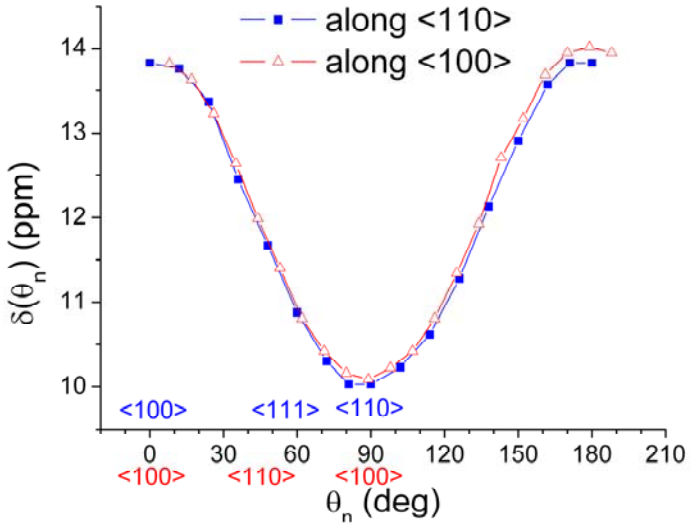

Figure S2. *Chemical shift $\delta(\theta_n)$ with different configurations between the external magnetic field and crystal orientation of Si substrate. The crystal orientation appeared in the x-axis becomes parallel to the external magnetic field while rotating the sample along <110> (upper) and <100> (lower) direction.*

S3. Variation of the chemical shift at different current densities

In order to confirm reproducibility of our measurement and find a variation of the chemical shift under a given current density, the angle resolved static NMR measurements were repeated a few times by making identical cells. A similar trend as shown in Fig. 4 was

found from the results (Fig. S3) of repeated experiments and the variation of the chemical shift is not large enough to disturb overall trend. The results are summarized in the Table S1, where the range of $\delta(0°) - \delta(90°)$ is about 2 ~ 4 ppm.

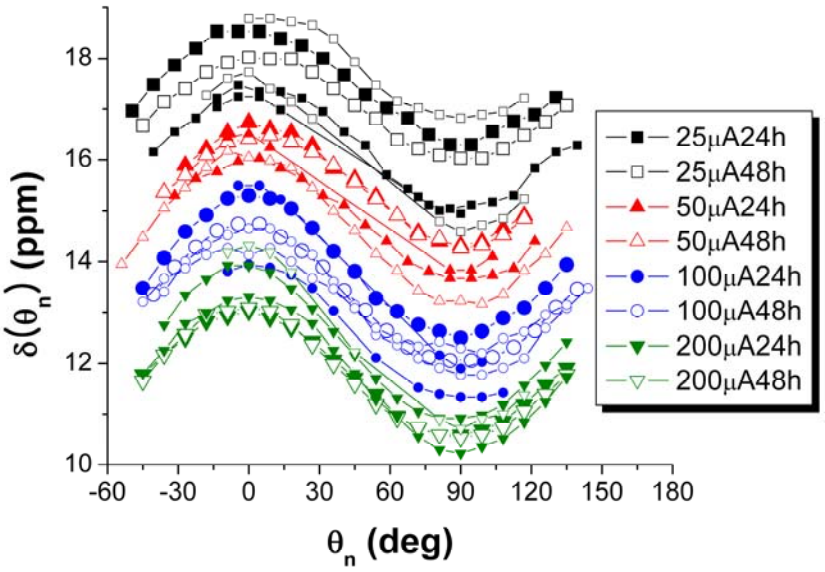

Figure. S3. *Results of repeated static NMR measurements. The curves marked by larger symbol are selected for the Fig. 4.*

Table. 1. *Summary of the results from repeated static NMR measurements. The cell #1 in each lithiation condition is selected for the Fig. 4.*

Condition	**Cell #**	$\delta(0°)$	$\delta(90°)$	$\delta(0°)-\delta(90°)$	δ_M	**Variation of** δ_M
25μA24h	**1**	18.5	16.3	2.2	17.0	15.7 ~ 17.0
	2	17.2	15.0	2.2	15.7	
	3	17.5	15.1	2.4	15.9	
25μA48h	**1**	18.0	16.0	2.0	16.7	15.6 ~ 17.5
	2	17.7	14.6	3.1	15.6	
	3	18.8	16.8	2.0	17.5	
50μA24h	**1**	16.7	14.3	2.4	15.1	14.46 ~15.13
	2	16.0	13.7	2.4	14.5	
	3	16.5	13.8	2.7	14.7	
50μA48h	**1**	16.5	14.3	2.2	15.0	14.2 ~15.0
	2	16.2	13.2	3.0	14.2	
100μA24h	**1**	15.3	12.5	2.8	13.4	12.2~13.4
	2	15.5	11.9	3.6	13.1	
	3	13.9	11.3	2.6	12.2	
100μA48h	**1**	14.7	12.1	27	13.0	12.7 ~13.0
	2	14.3	12.2	2.1	12.9	
	3	14.7	11.8	2.9	12.7	
200μA24h	**1**	13.0	10.6	2.4	11.4	11.3 ~11.9
	2	13.9	10.9	3.0	11.9	
	3	13.3	10.2	3.1	11.3	
200μA48h	**1**	13.1	10.5	2.6	11.4	11.4~11.9
	2	14.3	10.7	3.6	11.9	

S4. MAS NMR measurements for a ground sample

A silicon wafer was lithiated at a constant current density of 100 μA/cm^2 for 24 hours and it was ground in the glove box by using a porcelain pestle and mortar to make a powdered sample. Static NMR measurements were performed on the plates at $\theta_n \sim 54.7°$ before grinding and both static and MAS NMR measurements were performed on ground sample as preliminary experiments in this study. Grinding the sample influenced the linewidth and peak position as shown in Fig. S4. In static NMR spectrum on ground sample, the linewidth is much broader than that of the plate sample. The peak position located at 13 ppm in the static NMR spectrum for the plate sample is shifted to 18 ppm and an additional side peak at around 0 ppm appears. In addition, the MAS NMR spectrum for the ground sample is different from the spectrum taken for the plate sample (Fig. 6) under the similar spinning rates, indicating that unknown reactions may be involved during grinding. For this reason, an alternative method, horizontal stacking of small Li_xSi wafer pieces with SiO_2 particles in the rotor, was adopted for MAS NMR measurement.

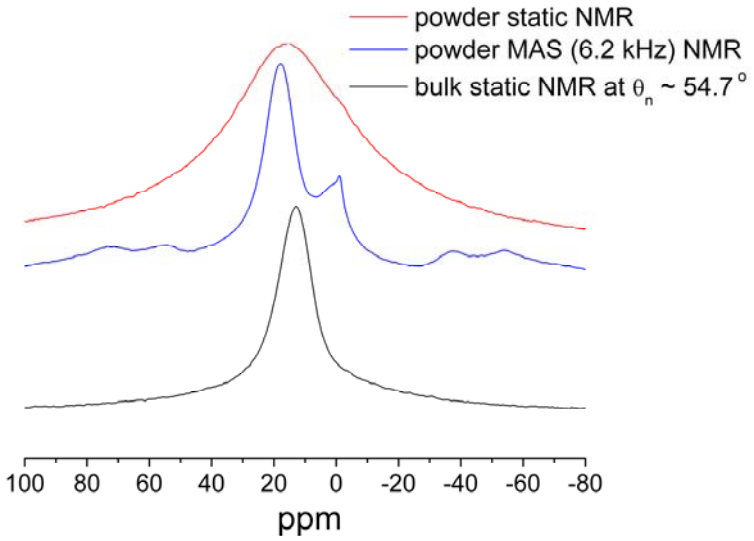

Figure. S4. *Bulk static NMR spectrum at* $\theta_n \sim 54.7°$ *, particles static and MAS NMR spectrum.*

S5. Unbalanced base line in the MAS spectra

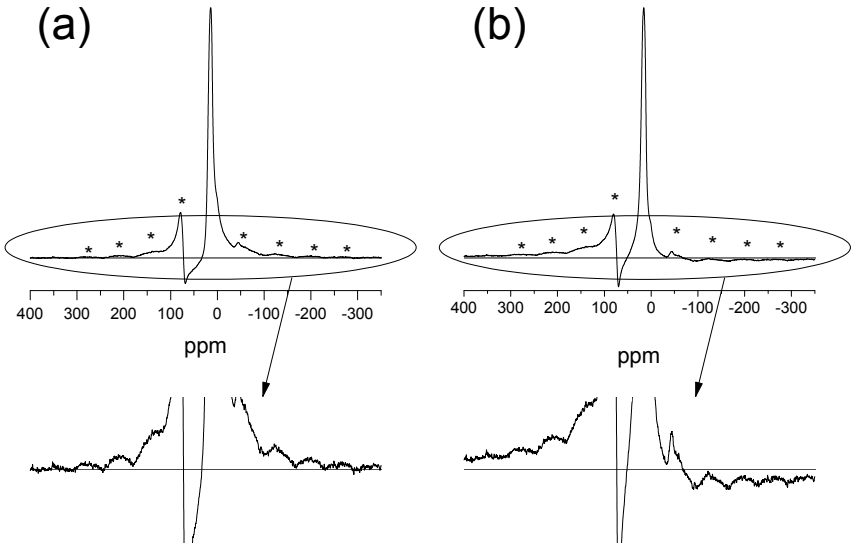

Figure S5. Spectrum obtained for 100μA24h sample with (a) symmetric overall base line; (b) asymmetric overall base line. Asterisk (*) means spinning side bands.

The spectrum in Fig. S5 (a) has a symmetric overall base line while in Fig. S5(a) it shows an asymmetric overall baseline. If a MAS spectrum, for example 100μA24h, is plotted in a large range of x-axis, a large and out of phase side band appears in the higher frequency region as shown in Fig. S5. Due to the large and asymmetric spinning side bands, it is difficult to adjust the phase that gives both symmetric overall base line for the spectrum and balanced base line for the main peak. If the receiver phase is adjusted so that the main peak becomes symmetric, the overall base line becomes asymmetric as shown in Fig. S5(b). In this study, we choose the receiver phase, which makes the overall base line symmetric even though the main peak is a little bit distorted by the side band as shown in Fig. S5(a).