In situ NMR Observation of the Formation of Metallic Lithium Microstructures in Lithium Batteries

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Supplementary Information:

Appendix: Theory Used to Quantify the NMR Signals of Metals.

For rf field of strength $\omega_1$, the field strength inside a metal ($\omega(x)$), at a depth $x$ from surface is given by,

$$\omega(x) = \omega_1 e^{-\frac{x}{d}}. \quad (1)$$

where, $d$ is the skin depth as defined in equation 1. For direct excitation NMR experiments, the NMR signal intensity ($S$) depends on the product of the strength of the applied rf ($\omega_1$) and duration of the rf pulse ($\tau_p$), via, $S \propto \omega_1 \tau_p$, where $\tau_p$ is chosen to satisfy $\omega_1 \tau_p = \pi/2$ in order to maximize the signal response. Since, inside a metal, the rf strength decreases as a function of the depth, we replace $\omega_1$ by $\omega(x)$ and write, $S \propto \int_0^\infty \sin(\omega(x)\tau_p)dx$ with $\omega(0) = \omega_1$. In the case of a typical metal electrode, the thickness of the metal ($c$) is far greater than the skin depth, and hence the upper limit of the integral can be set to infinity. The NMR signal from the entire volume of the metal, $S_{bulk}$ is,

$$S_{bulk} = s_o A \int_0^c \sin(\omega(x)\tau_p)dx \equiv s_o A \int_{\infty}^0 \sin(\omega(x)\tau_p)dx \quad (2)$$

where $A$ is the total surface area of the metal block and $s_o$ is the signal per unit volume of the metal. For $\omega(0)\tau_p = \omega_1 \tau_p = \pi/2$ (i.e, when we use a $\pi/2$ pulse to excite the signal), and using equation (1) we obtain from the above integration,

$$S_{bulk} = 1.3708 d A s_o \quad (3)$$

where, $S_{bulk}$ is the NMR signal from a metal block. For a metal block of length $a$, width $b$, and thickness $c$, $A = 2(ab + bc + ca)$ and the NMR signal intensity can be written as,

$$S_{bulk} = 1.3708 d \{2ab + 2(a + b)c\} s_o \quad (4)$$

To further simplify calculations we assume that the lithium metal electrode has only two types of morphologies, (i) bulk metal having a thickness far greater than skin depth, (ii) micro-
structures on the surface of the electrode, with a thickness that is much smaller than the skin
depth (i.e., the rf penetration of the dendritic whiskers is total). We also assume that the metal
electrode prior to electrochemical cycling has negligible micro-structure. If the total volume of
the lithium micro-structure is $V_\mu(t)$, then the NMR signal from the micro-structure ($S_\mu(t)$) can
be written as

$$S_\mu(t) = V_\mu(t) s_o$$  \hspace{1cm} (5)

and therefore, we can write from equation 4,

$$S = S_m + V_\mu s_o = s_o (V_{eff} + V_\mu) = s_o (1.3708 \, d \, A + V_\mu)$$  \hspace{1cm} (6)

The mass of lithium deposited at or stripped from ($M_{Li}(t)$) the metal lithium electrode can
readily extracted from the Electrochemical data:

$$M_{Li}(t) = C m_L \int_0^t I_c(t) dt$$  \hspace{1cm} (7)

where, $m_L$ is the mass of a lithium atom, $C$ is number of electrons per Coulomb, and $I_c(t)$ is the
current at time $t$. We assume 100% Coulombic efficiency, i.e, the loss of lithium due to the
formation of a SEI or another side reaction is negligible.

Note that since a typical discharge process results in stripping of lithium ions from the lithium
electrode under a negative value of current, the calculated mass could be negative in sign; i.e.,
the negative sign indicates a loss of observable mass from the electrode.

Supposing that the total mass deposited or stripped from the lithium electrode can be written as,

$$M_{Li}(t) = M_{SD}(t) + M_\mu(t)$$  \hspace{1cm} (8)

where, $M_{SD}$ is the mass of smoothly deposited or stripped metal and $M_\mu$ is the mass of the
micro-structure (mossy or dendritic lithium). If smooth deposition or stripping results in a change
of thickness of the metal by an amount $c_d(t)$, we can write,
\[ M_{SD}(t) = \rho_{Li} a b c_d(t) \] 

(9)

and assuming the volume of the micro-structure is \( V_\mu(t) \) we can write,

\[ M_\mu(t) = \rho_{Li} V_\mu(t) \] 

(10)

where, \( \rho_{Li} \) is the density of the lithium metal. Thus we obtain from equations 8, 9 and 10,

\[ M_{Li}(t) = \rho_{Li} a b c_d(t) + \rho_{Li} V_\mu(t). \] 

(11)

From equations 4 and 5, the total NMR signal originating from the bulk metal and the microstructures can be written as (where the original thickness of the metal electrode, that is the thickness before the stripping or deposition, is, \( c_o \)),

\[ S(t) = S_{bulk}(t) + S_\mu(t) = 1.3708 \ d \ {2ab + 2(a + b)(c_o + c_d(t))} s_o + V_\mu(t) s_o \] 

(12)

We denote the fractional change of NMR signal intensity \( I(t) \) as,

\[ I(t) = \frac{S(t) - S(0)}{S(0)} = \frac{2(a + b)c_d(t)}{A_o} + \frac{V_\mu(t)}{1.3708 \ d \ A_o} \] 

(13)

where, \( A_o = 2ab + 2(a + b)c_o \), is the area of the metal electrode before electrochemical cycling.

For comparison, we also calculate the dimensionless parameter \( I(t) \) for two extreme cases, (i) when we have a smooth deposition or stripping (\( I_{SD}(t) \)) and (ii) when all deposition or stripping results in microstructures (\( I_\mu(t) \)). For these two cases, from equations 8, 9, 10 and 13, we obtain,

\[ I_{SD}(t) = \frac{2(a + b)M_{Li}(t)}{A_o \rho_{Li} ab} \] 

(14)

and,

\[ I_\mu(t) = \frac{M_{Li}(t)}{1.3708 d \ A_o \rho_{Li}} \] 

(15)

We note that the right hand sides of equations 15 and 16 are expressed in terms of known or experimentally measured quantities.
Since, all parameters except $c_a(t)$ and $V_\mu(t)$ in the equations 12 and 13 are either known or can be measured experimentally, one can solve these two equations to calculate $c_a(t)$ and $V_\mu(t)$, and subsequently, by using equations 8-10, the masses $M_{SD}(t)$ and $M_\mu(t)$ can be calculated. Thus, the volume $V_\mu(t)$ and the mass $M_\mu(t)$ of the micro-structures formed during the electrochemical cycling can be estimated from the following experimental parameters: the intensities of the metallic Li NMR resonances (i) originating from the moss and lithium metal electrode during electrochemical cycling $S(t)$, and (ii) at the beginning of the in-situ experiments $S(0)$, i.e., in the pristine state, assuming no micro-structures have formed yet, (iii) the geometry of the lithium metal electrode (length $a$, width $b$, and thickness $c_o$). Other parameters such as the skin depth ($d$) and the density of the lithium metal ($\rho_{Li} = 0.51 \text{gcm}^{-3}$) are either known [15] or can be calculated as discussed earlier. It is important to note that the method discussed above does not require the NMR peaks originating from the bulk of the lithium electrode and the moss to be well resolved.

In order to confirm that the skin-depth must be taken into account, we have also derived appropriate expressions under the assumption that there is no skin-depth problem (in other words the extent of rf penetration is total for both the bulk metal and the micro-structures). We now define a dimensionless parameter $I_{vol}(t)$, which corresponds to the NMR signal intensity in a system where the signal is directly proportional to the volume (and thus mass) of the material; this can be calculated in a similar manner to equations 12 or 13,

$$I_{vol}(t) = \frac{S(t) - S(0)}{S(0)} = \frac{M_{Li}(t)}{\rho_{Li} abc_o}.$$  

(16)

The above formula can be compared with the experimentally measured values of $I_{expt}(t)$.

So far we have derived the relevant expressions of NMR signal intensity originating from a single lithium metal electrode subjected to electrochemical cycling. Now we shall also consider a type of cell where both the electrodes are lithium metal strips (a symmetric cell). For a symmetric cell net transfer of mass of lithium from one electrode to the other at any given point of electrochemical cycling is zero, since the loss of mass from one electrode results in an equal gain of mass by the other electrode, that is, $M_{Li}(t) = 0$ (as before, we assume that the loss of
lithium in forming the SEI is negligible). Therefore, in the absence of the skin depth issues NMR signal originating from a symmetric cell will remain constant during the electrochemical cycling. Also, smooth deposition/stripping processes at both electrodes will result in constant NMR signal since the change in thickness $c_d(t)$ will be equal and opposite in sign for both the electrodes. Hence we can write for a symmetric cell,

$$M_{Li}(t) = I_{SD}(t) = I_{vol}(t) = 0.$$  \hspace{1cm} (17)

However equations 8-13 can still be applied for symmetric cells. From equation 9 we obtain $M_{\mu}(t) = -M_{SD}(t)$, which represents the growth of lithium microstructure that occurs at the expense of the loss of smoothly deposited lithium. Note that the errors introduced by any loss of Li metal due to SEI formation or other side-reactions will lead to an underestimation of the extent of microstructure formation, in systems with significant SEI formation. However, SEI formation can be readily monitored in the in situ NMR experiment via the formation of diamagnetic Li$^+$ species with resonances close to 0 ppm. Thus, this effect can be easily corrected for by monitoring the evolution of the intensities of the lithium-NMR signals of the diamagnetic components, since these are directly related to the mass of these species. The total mass of lithium/Li$^+$ remains constant in the cell, and thus the sum, $M_{Li} + M_{SEI} + M_{electr}$, where $M_{SEI}$ and $M_{electr}$ are the masses of lithium in the SEI and electrolyte, respectively, remains unchanged.

**Analysis of the Li metal signal in a Li:Silicon Cell**

Here the first change involves insertion of Li into silicon, and the loss of Li from the negative electrode [1]. However, the Li metal signal remains essentially unchanged on charging, consistent with smooth stripping from the bulk Li strip (Figure S1). On charge, however, a significant increase in Li metal signal occurs, so that the apparent Li mass after one cycle has increased noticeably, indicating that the Li electrode that is formed after on cycle is now mossy/dendritic. There is a large irreversible capacity loss in the 1st cycle, however, this has no effect on the phenomenon under investigation. The following 2nd discharge (not shown) continues by removal of primarily the mossy/dendritic lithium.
Figure S1: (a) Spectral snapshots of the $^7$Li metal signal. (b-c) Current and voltage profiles. (d) Li signal intensity (fractional change, $I_{\text{expt}}$, normalized to the signal at the beginning). The Li intensity remains essentially constant during discharge (Li stripping). Since uniform stripping leaves the electrode area unchanged and the change in thickness is negligible, the signal remains virtually constant. The minor changes in the signal intensity during the 1st discharge are most likely due to the formation of pits which will are smoothed out or removed as stripping continues.

References: