

Planning report for Master's thesis about nucleation of lithium on different substrates

Gottfrid Olsson

2024-02-07

Introduction, background and theory

Batteries play an important role in today's society, being used in things from bicycle lamps and mobile phones to pacemakers and electrical vehicles. Lithium-ion batteries are one of the most common type of batteries and have a relatively high specific energy. A battery's energy content is determined by the material in the two electrodes, which in a lithium-ion battery often is graphite for the anode and LiCoO_2 for the cathode. The specific energy can be increased significantly by replacing the graphite (372 mAh g^{-1}) with lithium-metal (3861 mAh g^{-1}). However, an anode of lithium (Li) can cause problems. When Li-ions recombine with electrons to form Li-metal, the growth of Li-metal on the anode surface can be uneven. Uneven plating is unfavorable because it affects the cell's performance negatively, for example through lowered Coulombic efficiency, which leads to a shorter lifetime [1]. It is important to have deep knowledge about the nucleation of Li-metal to be able to prevent uneven plating of Li in future battery cells.

The process of nucleation consists of several steps, as shown in Figure 1. First, the solvation shell of a solvated Li-ion is released. The Li-ion then recombines with an electron from the substrate and becomes a Li atom. Several Li atoms combine to form a cluster, or nuclei. Small nuclei are thermodynamically unstable and only become stable and can reliably grow once they reach a certain size, a critical nuclei radius [2]. The nucleation process can be modelled with nucleation theory.

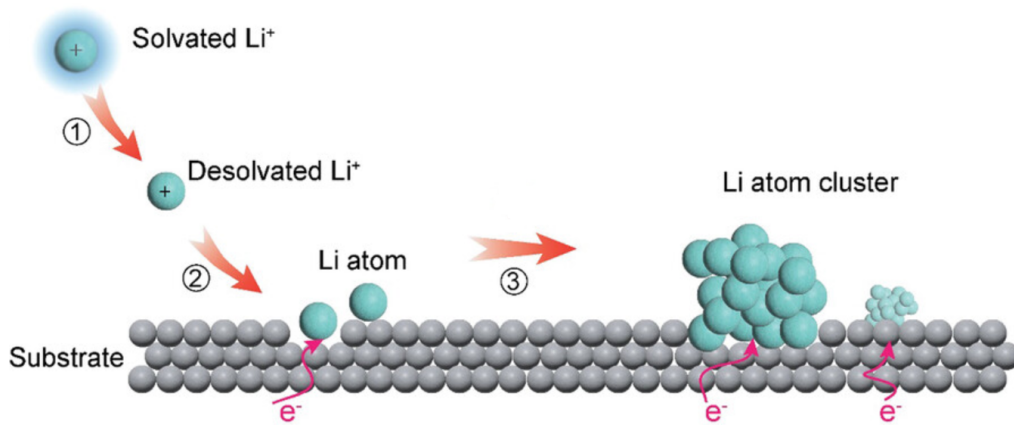


Figure 1: Schematic representation of the nucleation steps. Figure from [2].

Classical nucleation theory starts with thermodynamics, specifically the change in Gibbs free energy. Gibbs free energy, G , describes the maximum amount of work a closed system can do that is not pressure-volume work. This is relevant because the change in Gibbs energy, ΔG , for a reaction dictates whether that reaction can occur spontaneously, if $\Delta G < 0$, or require external energy to happen, if $\Delta G > 0$. In general terms, when a solid phase is created from a supersaturated solution (a solution in which the concentration of solutes is larger than the stable concentration at those conditions), there is a gain in energy from creating bulk ($\Delta G_{\text{bulk}} < 0$) and at the same time a cost for creating surface ($\Delta G_{\text{surface}} > 0$). This can be written as

$$\begin{aligned}\Delta G_{\text{nucleation}} &= \Delta G_{\text{surface}} + \Delta G_{\text{bulk}} \\ &= A\gamma + V\Delta G_V \\ &= 4\pi r^2\gamma + \frac{4}{3}\pi r^3\Delta G_V\end{aligned}$$

where A is the surface area created, γ is the surface energy of the Li-electrolyte interface, V is the volume created, ΔG_V is the change in Gibbs energy per created volume, and in the last line we assume that the nuclei is spherical with radius r . The overpotential for deposition, η , is related to Gibbs energy as [3]

$$\Delta G_V = -\frac{F|\eta|}{V_m}$$

where F is Faraday's constant and V_m is the molar volume of the element creating the nuclei (here Li). Figure 2 shows how Gibbs free energy is related to the process of nucleation of Li and overpotential. A larger overpotential means that the Li-ion and electron have more energy, meaning there is a smaller energy barrier for nucleation.

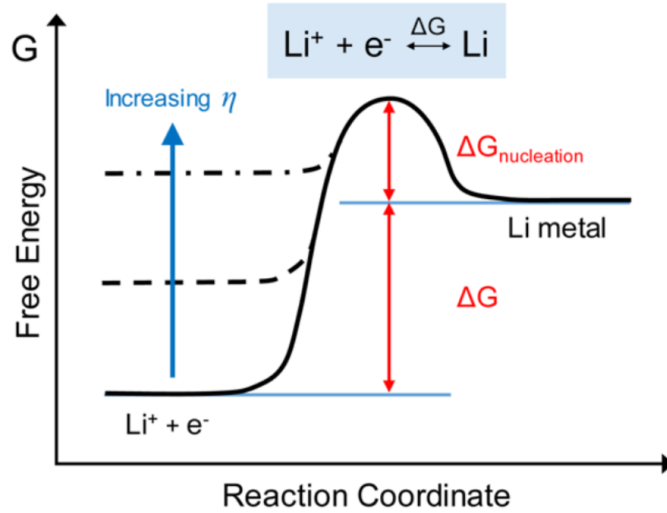


Figure 2: Schematic representation of Gibbs energy during the reaction of nucleating Li metal from Li-ions and electrons. Figure from [3].

The critical radius of nucleation, r_{critical} , at which the nuclei start being thermodynamically stable and grow is given by [3]

$$r_{\text{critical}} = \frac{2\gamma V_m}{F|\eta|}.$$

From this we see that the size of the nuclei is inversely proportional to the overpotential, $r \propto \eta^{-1}$. One can show¹ that the areal nuclei density, number of nuclei per area, is proportional to the overpotential to the third power, $N \propto \eta^3$. These two relations dictate the nuclei distribution as function of overpotential, and is shown in Figure 3. These theoretical relations have been supported by experimental data [3].

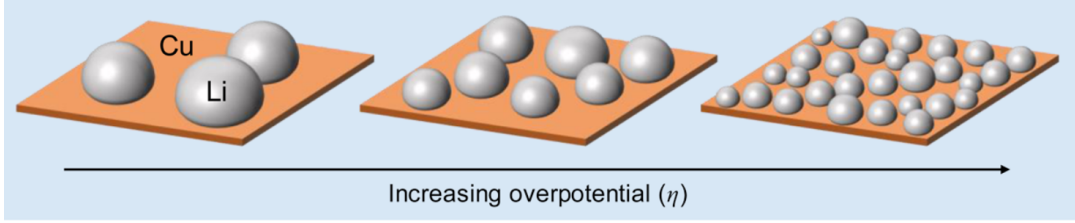


Figure 3: Schematic representation of the nuclei size distribution as function of increasing overpotential. For lower overpotential, the nuclei become fewer and larger, while larger overpotential results in more but smaller nuclei. Figure from [3].

Furthermore, it has been shown that the nucleation occurs more or less instantaneously, followed by a longer period of growth [3]. This is shown in Figure 4, where the nucleation occurs quickly at a larger overpotential, $|\eta_n|$, compared to the longer growth (plateau) region for which a smaller overpotential, $|\eta_p|$, is required.

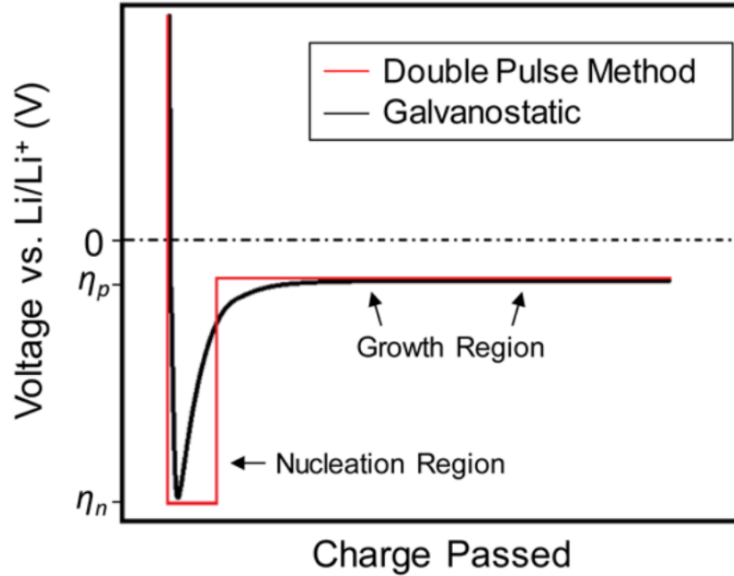


Figure 4: Two regions representing nucleation and then growth during galvanostatic (constant current) deposition. Figure from [3].

Many things have been investigated regarding the nucleation and growth of Li-metal. Some examples include how the form of the nucleated Li-nuclei depends on pressure [1],

¹Given that $r_c \propto \eta^{-1}$, we can show that the areal nuclei density is proportional to the third power of the overpotential, $N \propto \eta^3$. We start by defining some terms. Let n be the number of nuclei, V be the total deposited volume, r be the radius of the nuclei, and A be a fixed area on which we calculate N . Next, we reason that $V = nr^3$ because the total volume deposited is the number of nuclei times their volume (assuming spherical nuclei), which gives $n = V/r^3$. Since we seek $N = n/A$ we put together the relations we have just written down to get $N \propto n \propto r^{-3} \propto \eta^3$, where $r \propto \eta^{-1}$ was used in the final step. Finally, we arrive at the two conclusions that $r \propto \eta^{-1}$ and $N \propto \eta^3$, in agreement with [3].

plating of Li on copper with different current densities and areal capacities [3], and how the nucleation is affected by the substrate's surface area and morphology [4]. This work will contribute with scientific knowledge by using electron microscopy to image the Li-nuclei as function of current density and areal capacity, for several different substrates.

Preliminary aim

The purpose of this work is to investigate how the nucleation in Li-metal cells depend on the substrate, current density, and areal capacity. Since the nucleation affects the following growth of Li-metal, more knowledge about the phenomena can lead to ways of enabling more even and regular nucleation and growth in Li-metal batteries, which would improve the performance.

Objective

This work intends to answer the fundamental scientific question: "How does the size distribution of the Li-nuclei depend on the substrate, current density, and areal capacity?". The size distribution can be specified through a histogram as well as relevant statistical measures such as mean, median, mode, and standard deviation.

Scope and limitations

This work intends to investigate cells at room temperature and atmospheric pressure with:

- One electrolyte
- Different substrates
- Different current densities (mA cm^{-2})
- Different areal capacities (mAh cm^{-2})

Substrates can be chosen based on how well Li wets the surface. Specifically, can the change in enthalpy for an infinite dilute solution of Li and a metal, ΔH_{mix} , be used. The value of ΔH_{mix} indicates whether Li-metal shows uniform wetting and uniform growth or uneven, island-like, plating [4]. Examples of metals with negative ΔH_{mix} are Au (-113 kJ mol^{-1}), Pt (-96), Ag (-55), Si (-46), Zn (-26), Cu (-19) och Al (-13), while metals with positive value are Mo (169), W (169), Ti (130), Cr (131), Fe (94) och Ni (3) [4]. I propose to investigate at least one metal with large positive value (Mo, W, Ti, or Fe) and one metal with ΔH_{mix} around zero (Ni, Al, or Cu). Elements with large negative value are excluded due to their tendency to create an alloy with Li, a process which lies outside the scope of this study. A concrete proposal of elements are W, Fe, Cu, Ni, and glassy carbon². The chosen electrolyte is 4 mol L^{-1} bis(fluorosulfonyl)imide (LiFSI) solved in dimethoxyethane (DME), due to favorable (nearly circular) Li growth in this electrolyte [3].

The supervisor recommended examining current densities of varying orders of magnitude. A starting point could be 0.01 Ah cm^{-2} , 0.1 Ah cm^{-2} , 1.0 Ah cm^{-2} , and 10 Ah cm^{-2} . Which areal capacities that are interesting will have to be determined later, and a starting value could be around 0.1 mAh cm^{-2} , based on the text to Figure 2 from [3]. Note that the

²My supervisor wishes to investigate glassy carbon.

plated areal capacity should be taken as the amount of plated Li after the SEI-layer have been formed.

Methods and execution

Experimental methods and equipment required are available at the department of physics (material physics) and the department of industrial and materials science (IMS). Material physics have laboratories for production and cycling of cells, while IMS has a scanning electron microscope (SEM) where cells containing Li is allowed. The supervisor will instruct about the cell production and cycling, and also assist with a license for use of the SEM.

The execution, in broad brushstrokes, are:

- Planning report
- Training of equipment and methods in the laboratories
- Production and cycling of cells
- Imaging with the SEM
- Data analysis: size distribution of the Li-nuclei
- Analysis and answering the scientific question

Documentation and writing of the final report will take place continuously during the project.

A note about the cycling of the cells. When the cells are cycled for plating of Li before imaging with the SEM, a two-electrode setup is sufficient. However, to be able to separate the electrodes individual contributions to the potential of the cell, a setup of three-electrodes must be used. This is, for example, important when determining the overpotential of the nucleation [5].

Time plan

A first draft of the time plan is shown on the next page and is divided based on the main areas of the work: planning report, reading of literature, experimental work, data analysis, final report, and presentation. Because this is my first time carrying out this type of experimental work with batteries, the time plan is my best guess, or wish. In reality, I expect that things take more time than imagined, which is why a few weeks towards the end is quite loosely planned such that they can act as time buffers if need be.

[illegible]

Social, ethical and ecological aspects

This work will not have to take into account social, ethical, or ecological aspects since the fundamental scientific question will be answered through experiments with battery cells. Thus, aspects such as anonymity, ethical handling of personal data and the like are in this context irrelevant.

References

- [1] C. Fang, B. Lu, G. Pawar, M. Zhang, D. Cheng, and S. Chen, “Pressure-tailored lithium deposition and dissolution in lithium metal batteries,” *Nature Energy*, vol. 6, pp. 987–994, 2021-10. DOI: 10.1038/s41560-021-00917-3.
- [2] Y. Xu, K. Dong, Y. Jie, *et al.*, “Promoting mechanistic understanding of lithium deposition and solid-electrolyte interphase (sei) formation using advanced characterization and simulation methods: Recent progress, limitations, and future perspectives,” *Advanced Energy Materials*, vol. 12, no. 19, p. 2200398, 2022. DOI: <https://doi.org/10.1002/aenm.202200398>.
- [3] A. Pei, G. Zheng, F. Shi, Y. Li, and Y. Cui, “Nanoscale nucleation and growth of electrodeposited lithium metal,” *Nano Letters*, vol. 17, no. 2, pp. 1132–1139, 2017-01. DOI: 10.1021/acs.nanolett.6b04755.
- [4] W. Liu, P. Liu, and D. Mitlin, “Tutorial review on structure - dendrite growth relations in metal battery anode supports,” *Chemical Society Reviews*, vol. 49, pp. 7284–7300, 2020-10. DOI: 10.1039/d0cs00867b.
- [5] A. Mohammadi, L. Monconduit, L. Stievano, and R. Younesi, “Measuring the nucleation overpotential in lithium metal batteries: Never forget the counter electrode!” *Journal of The Electrochemical Society*, vol. 169, no. 070509, 2022. DOI: 10.1149/1945-7111/ac7e73.