Less is More: A Perspective on Thinning Lithium Metal Towards High-Energy-Density Rechargeable Lithium Batteries

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Table S1 The definition of Li foils' thickness in previous literatures

The thickness of Li foils/μm (the areal capacity of used Li)	The description/definition of the thickness of Li foils	Reference
400 (80 mAh/cm^2)	thick	J. Phys. Chem. C, 2018, 122, 21462−21467
10 (2 mAh/cm^2)	thin	
100 or 50	thick	Nat. Energy, 2021, 6, 723-732
20	thin/ultrathin	
125	thick	Chem. Commun., 2015, 51, 17100
30	thin	
50	ultrathin	Adv. Mater. 2019, 31, 1902785; Energy Environ. Mater. 2020, 3, 160–165
30	very thin	Batteries & Supercaps 2020, 3, 1370–1376
< 50	thin	Proc. Natl. Acad. Sci. U.S.A., 2020, 117, 27195-27203
10-20	ultrathin	Nat. Commun., 2019, 10, 4930
> 100	thick	ACS Appl. Mater. Interfaces, 2018, 10, 16521−16530
40	thin	
20	ultrathin	Adv. Energy Mater., 2021, 11, 2003769
0.5 - 20	ultrathin	Nat. Energy, 2021, 6, 790-798
50 - 100	very thick	Nano Lett., 2022, 22, 3047-3053
< 15	ultrathin	
10 - 50	ultrathin	Adv. Energy Mater., 2021, 11, 2102259
1 - 30	ultrathin	Chem. Eng. J. Adv., 2022, 9 100218
15	ultrathin	Adv. Mater., 2021, 2005305
< 30	ultrathin	Nano Energy, 2020, 74, 104817

Table S2 Thin Li fabrication techniques and their corresponding details

This is presented as an independent table in the supplementary information.

Note 1 The correspondence of a Li metal anode thickness and its areal capacity

As we know, metallic Li at normal temperature (20 °C) and pressure (101.325 kPa) possesses a density (ρ) of 0.534 g/cm^3, and a theoretical gravimetric capacity of ~ 3860 mAh/g. Accordingly, we can obtain the theoretical volumetric capacity of 2061.24 mAh/cm^3. Thus, an areal capacity of ~ 1 mAh/cm^2 corresponds to a thickness of 1/2061.24 cm, namely 4.85 μm. Here, for the convenience of memory, we say 5 μm is equivalent to ~ 1 mAh/cm^2.

Note 2 The correlation between cycle life and the thickness of LMAs and corresponding CE_{avg} of a battery

Here, we assume a battery consists of an Li metal anode of various thickness and a Li-containing cathode with an areal capacity of 4 mAh/cm^2. First, we assume charging to 100% state-of-charge, and the possible Li loss occurs only at the Li metal anode side. In this case, the capacity passed per cycle ($Q_{Li\ passed\ per\ cycle}$) is equivalent to the cathode capacity ($Q_{cathode,}$ namely 4 mAh/cm^2) if there are extra Li in anode side to compensate for Li losses. We define the battery reaching its end when it runs out all of the Li from the Li-metal anode (Q_{Li}) and 20% of the Li from the cathode ($Q_{cathode}$) after n cycles. Then we can calculate the averaged Coulombic efficiency (CE_{avg}) for Li plating/stripping processes on the anode side as follows:

$$CE_{avg} = 1 - \left(\frac{Q_{Li} + 0.2Q_{cathode}}{n}\right) \times \left(\frac{1}{Q_{Li\ passed\ per\ cycle}}\right) = 1 - \frac{Q_{Li} + 0.2Q_{cathode}}{nQ_{cathode}}$$

Among which, the term (Q_{Li} + 0.2$Q_{cathode}$)/n represents the average Li loss per cycle.

On this basis, we then define the fraction of Li passed per cycle (F_p) as follows:

$$F_p = \frac{Q_{cathode}}{Q_{cathode} + Q_{Li}}$$

Combining the above two equation, we can get a relation between (F_p) and cycle life (n), namely

$$F_p = \frac{1}{n(1 - CE_{avg}) + 0.8}$$

Based on this equation, we can calculate the cycle life of Li meta batteries with anodes of different thickness. For example, when we have a 50 μm Li metal anode (5 μm is almost equivalent to 1 mAh/cm^2) and a CE_{avg} of 80%, then we can get a F_p value of 4/14 and a cycle life of 13.5.

For more detailed process, please refer to the article of Zhu et al (*Proc. Natl. Acad. Sci. U.S.A.*, 2020, 117, 27195-27203).