

Thickness effect

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1 Overpotential

To investigate the utilization of the cathode, it's essential to understand the discharging process therein. On a microscopic scale, at each of the active particles, the rate of intercalation is a function of the overpotential η , where $\eta < 0$ corresponds to a net positive cathodic current (lithium intercalating into the active material in the cathode) and $\eta > 0$ corresponds to a net positive anodic current (lithium de-intercalating from the active material in the cathode). The overpotential is given by

$$\eta = \Delta\phi - U \quad (1)$$

These different variables are defined as follows:

- $\Delta\phi = \phi_s - \phi_l$ is the potential difference across the liquid-solid interface at the active particle. It depends on the applied potential V across the cell and the resistive losses for the electrons traveling through the cathode and the lithium ions traveling through the electrolyte from the anode to the cathode. The resistive losses from the solid phase are negligible compared to those from the liquid phase. $\Delta\phi$ increases with increasing applied voltage V but will decrease from the cathode surface to the current collector because of the increasing potential in the liquid phase. This is due to the resistive losses in the liquid.
- U is called the open-circuit potential. It is the potential difference across the local interface which would result in a net zero intercalation rate. U is a material dependent function which in turn depends on the local lithium concentrations in the electrolyte, c_l , and at the surface of the active particle, c_s . U increases when c_l increases and decreases when c_s increases. A high U causes a higher cathodic current. U is also often defined on the cell level as the applied voltage where the net cell current is zero. However, it's important to note that net zero current on the cell level does not mean that there are no currents in the cathodes, only that they cancel out. In the present discussion U will refer to the local open-circuit potential. U is also often defined as a material property of the active material, measured relative a reference potential. In the present discussion, however, U is the open-circuit potential at the local interface relative the local electrolyte.

The essential message here is that there is a local overpotential $\eta = \eta(c_l, c_s, V)$ that determines the magnitude of the intercalation rate. In the cathode during discharge, η is negative and a larger magnitude (more negative) corresponds to a faster intercalation rate. η decreases (more negative) with decreasing V , decreasing c_s , and increasing c_l . In other words, a location with a high electrolyte concentration and low active material concentration will result in intercalation at a higher applied voltage. Conversely, a location with low electrolyte concentration and high active material concentration will require a lower applied voltage to drive the intercalation. The intercalation rate increases exponentially with the overpotential, but locally the overpotential is very small and the local intercalation rate is approximately proportional to the local overpotential, $i \propto \eta$.

2 Galvanostatic Discharge Process

In a galvanostatic discharge process, the applied voltage is varied to maintain a constant current at the cell level. The discharge is stopped when the applied voltage drops below a threshold voltage to prevent side reactions. This happens when, everywhere, c_l is too low and/or c_s too high, requiring a very low V to maintain the constant cell current. In a thin cathode this happens when c_s is high everywhere. In a very thick cathode, there will be a deeper region with low c_l and a surface region with high c_s , neither of which will produce an appreciable intercalation rate. In this cathode, the voltage threshold is reached when the intermediate region shrinks to the point where the participating surface area is too small to maintain the cell current. In the following, I will describe the discharge process step by step.

2.1 The First Minute

At the start of the discharge process, the porous cathode is filled with electrolyte with a lithium concentration of around 1 M and active particles with low lithium concentration. As soon as the voltage is applied, the initial lithium starts to intercalate into the active particles. The initial lithium in a $50\mu\text{m}$ cathode with a porosity of 30%, filled with 1 M Li^+ , is enough for 0.04 mAh/cm^2 if it was fully intercalated. At 2 mA/cm^2 this is enough to last for 72 s. If the cathode has a volumetric nominal capacity of 440 mAh/cm^3 (corresponding to a active material specific capacity of 220 mAh/g and active material density in the cathode of 2 g/cm^3), the initial electrolyte is enough to last for 66 s at a discharge current of 1C, for a cathode like this of any thickness. The large surface area participating in the intercalation means that the discharge current can be maintained with a small overpotential (and high applied voltage), despite the fact that the initial lithium concentration in the electrolyte will drop to zero within about a minute, in turn decreasing U substantially.

During this first minute, lithium is diffusing into the cathode from the separator. Initially, this is a slim region with a high lithium concentration. The open-circuit potential is high here and a high intercalation current is produced, but because of the small volume, it only produces a fraction of the total current in the cathode. This fraction will grow quickly as the diffusing lithium reaches further.

The speed of the front of this incoming lithium depends both on the diffusion coefficient of the lithium in the electrolyte, as well as how much lithium is removed from the electrolyte between the separator and the lithium front. Initially the speed is relatively fast, but as it progresses, a larger fraction of the total current is produced at the surface (rather than from the initial electrolyte in the bulk of the cathode), slowing down the lithium front. In addition, as the active particles fill up with lithium they expand, constricting the passage of the electrolyte and reducing the effective diffusion coefficient. At some point, within a minute or so, virtually all of the intercalation current is produced at the region closest to the cathode surface.

It should be noted that it may very well be that the diffusion is fast enough for the initial electrolyte not to play any limiting role in the initiation of the discharge process. This would mean that the shift from intercalation in the bulk to the intercalation at the surface happens much quicker than the time it would take to consume all that initial lithium. This could be the case either because the diffusion is fast and/or because the initial local electrolyte concentration is much higher than 1M, as is likely the case immediately after a charge. In addition, it would mean that there remains a baseline lithium concentration in the electrolyte throughout the cathode that is decreasing very slowly over the course of the discharge.

2.2 Quasi Steady-State Until End of Discharge

At this point, the region between the cathode surface and the diffusion front is producing all of the discharge current and a steady influx of lithium from the separator has been established. As the discharge progresses, the active particles at the surface fill up, increasing c_s , decreasing U , decreasing the intercalation rate, and decreasing the local effective diffusion coefficient (due to expanding particles). Now there are three zones in the cathode: A *surface zone* closest to the cathode surface with a low intercalation rate (due to high c_s) and effective diffusion coefficient; a *depletion zone* closest to the current collector with near zero intercalation (due to low c_l); and a *reaction zone* in between, where most of the current is produced (due to low c_s and high c_l).

The growth rate of the surface zone is determined by the overall intercalation rate, which is proportional to the discharge current. The speed of the diffusion front (the boundary delimiting the reaction and depletion zones) is determined by the rate of diffusion of the ions through the surface zone and the reaction zone. Since the surface region is growing, the overall ionic resistance through the surface region grows, slowing down the diffusion front. At some point, the growth of the surface region will exceed the speed of the diffusion front, causing the reaction zone to shrink. As the reaction zone shrinks, the total surface area actively participating in the discharge is reduced and the applied potential V has to be reduced further to maintain the constant current. If the cathode is thick enough, the reaction zone will shrink until V is reduced to the threshold voltage, at which point the discharge ends. In this case, the active material in the depletion zone remains unused. On the other hand, if the cathode is thin, the diffusion front may reach the current collector before the surface zone catches up to it. Subsequently, the reaction zone will shrink as it is squeezed between the surface zone and the current collector (rather than the diffusion front). When the reaction zone becomes small enough (and c_s becomes large enough) to require an applied voltage below the threshold voltage, the discharge ends. In this case, most of the nominal capacity of the cathode is utilized. The depth the discharge reaches will be referred to as the *penetration depth*, and the case where the penetration depth is shorter than the cathode thickness will be referred to as a *diffusion-limited discharge*.

2.2.1 Some supporting evidence

Figure 1, shown below, is taken from a 2017 article by T. Nakamura et al. [1]. In that article, they sandwiched a cathode between an aluminum current collector and a polyamide film. Then they charged it while letting electrolyte enter through one of the edges (fig. 1b). This serves as a model for a semi-infinite cathode. After charge, they used X-ray absorption spectroscopy(XAS) to map the lithium content in the active particles. Figure 1c shows the XAS maps before charge and after charging at different current densities. Blue indicates discharged(high c_s) and red indicates charged(low c_s). Figure 1a shows the cell voltage as a function of specific charge capacity during the three charges.

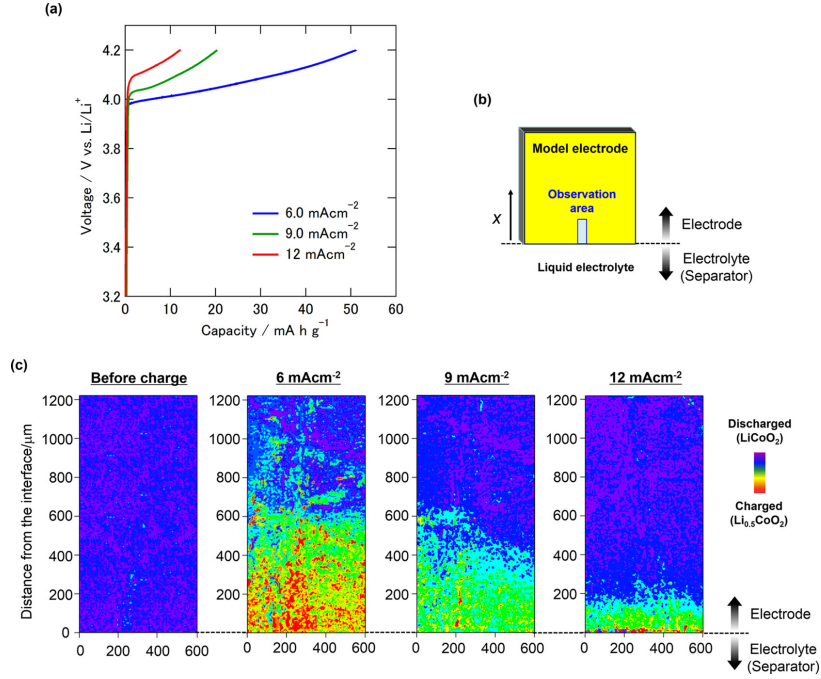


Figure 1: Subfigure (c) shows an X-ray absorption spectroscopy mapping of concentration intercalated lithium before and after charge at different current densities. The planar model cathode is shown in (b), and the charge curves are shown in (a). Figure from Ref. [1].

There are two important differences between this study and the discharge process I described above:

1. T. Nakamura's study describes a charge process, rather than a discharge process. However, the same reasoning used for the discharging case also applies to the charging process, by inverting the signs of all changes to η , V , c_s , and c_l .
2. Due to their sandwich model, the process has the diffusion directed parallel to the current collector. This means that the electronic resistance of the cathode is independent of the distance from separator. In a coin cell or pouch cell, the applied potential is a gradient across the thickness of the cathode due to electric resistance. This gradient contributes to a higher intercalation rate closer to the current collector, but is almost completely flooded by the much larger opposite effect of the ionic conductivity in the electrolyte. Consequently, the electronic resistance is a minor contributor to potentials involved in a diffusion-limited charge.

Despite these caveats, there is basic information to be extracted from these results:

1. At all current densities, three zones have formed: A charged zone close to the separator, a discharged region at a greater depth, and a transition zone in between the two.
2. As current density is increased, both the charged region and the transition region shrinks, and the charging specific capacity is reduced.

These are things you would expect in a diffusion-limited charge as described above. In discharges at higher current densities the growth rate of the surface region is greater, causing the discharge to end at an earlier time and charge capacity.

3 Utilization of the Cathode

A higher discharge current has two effects:

1. The overpotential required to maintain the current is decreased (more negative), causing the threshold voltage to be reached when the reaction zone is larger than it would have been otherwise.
2. The growth rate of the surface region is increased.

Consequently, if one were to discharge the battery at a higher constant current, if the current is low enough to allow the diffusion front to reach the current collector, the utilization of the cathode will decrease due to the first item in the list. If the discharge current is high enough to end the discharge before the diffusion front reaches the current collector, the second item will cause the discharge to end at a smaller penetration depth and with a larger depletion zone. The remaining depletion zone at the end of discharge is wasted and does not contribute to the energy density of the battery. In order to increase the energy density of a battery cell you can increase the cathode thickness, but to utilize that energy the discharge current needs to remain low enough for the full cathode to be utilized. This optimal relationship between current density and cathode thickness is an important parameter when designing batteries. The utilization of the cathode, Λ , is defined here as the fraction of the maximum capacity that can be discharged at a given current density:

$$\Lambda = \frac{Q_{\text{discharge}}}{Q_{\text{max}}}. \quad (2)$$

The maximum capacity, Q_{max} , is the capacity that can be extracted at an infinitesimal current density. For practical reasons, the maximum capacity is approximated with the capacity extracted at a very low current density, e.g. C/10. At low discharge currents the utilization is close to 100%, but as the discharge current is increased to the point of a diffusion-limited discharge, the utilization will begin to decrease. Conversely, if one were to measure the utilization of cathodes with different thicknesses but with the same current density, one would find that the cathodes with thicknesses larger than the penetration depth will have a decreasing utilization with increasing thickness. This is because the penetration depth is largely independent of the cathode thickness, and any thickness beyond the penetration depth increases Q_{max} without increasing $Q_{\text{discharge}}$. As a simplified picture, consider a final state of charge profile where the cathode is 100% discharged up to the penetration depth, and 0% discharged in the depletion zone. In such a case, the dependence of utilization on cathode thickness can be expressed with

$$\Lambda = \begin{cases} 1 & \text{for } L \leq L_p \\ \frac{Q_A \cdot L_p}{Q_A \cdot L} = \frac{L_p}{L} & \text{for } L > L_p \end{cases} \quad (3)$$

where L is the cathode thickness, L_p is the penetration depth, and Q_A is the areal capacity at very low discharge currents (approaching maximum capacity). The utilization of a cathode like this is plotted in figure 2 at three different penetration depths, corresponding to three different current densities. For thinner cathodes, the utilization is full, but as the thickness is increased, the utilization

drops with L^{-1} . In addition, higher current densities will reduce L_p . These are general trends we expect to see in a cathode as the thickness is increased past the penetration depth.

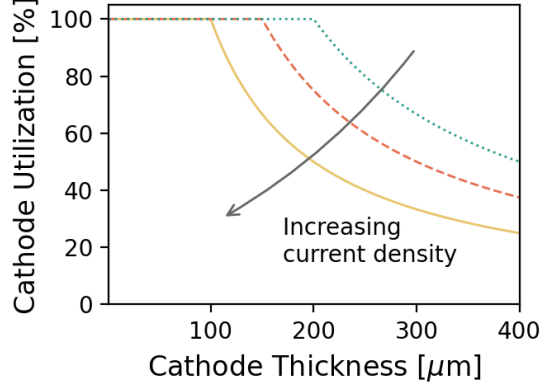


Figure 2: An idealized depiction of how the cathode utilization changes as the cathode thickness increases and as the discharge current increases. The utilization is full for cathodes with a thickness smaller than the penetration depth. At thicknesses beyond the penetration depth, the utilization drops with the inverse of the cathode thickness. The penetration depth decreases with increasing current density.

In real cathodes after discharge, the state of charge profile is not a sharp drop from 100% utilization to 0% utilization. Instead, it is a broader transition. This is clearly seen in the XAS mapping in figure 1 [1]. This breadth of this transition will smooth out the sharp edges shown in figure 2. In addition, the increase in current will not only reduce the penetration depth, but also the utilization of the zones that are "fully" discharged, due to increased resistances and other limitations. But these effects are largely independent of thickness, and would cause a drop in utilization across all thicknesses as the discharge current increases.

Figure 3 shows how this thickness effect manifests in real data. Figures 3a and 3c show the specific discharge capacity for a series of LFP cathodes of different cathode thickness across a series of current densities, taken from D.Y.W. Yu's 2006 and H. Zheng's 2012 studies, respectively [2, 3]. The specific discharge capacity is the total discharge capacity divided by the total mass of active material in the cathode. At low current densities, the cathodes have the same specific capacity (~ 150 mAh/g) regardless of thickness. This is because the full cathode is participating in the discharge, and the mass of active material is proportional to thickness. Taken together it means that the discharge capacity is proportional to the thickness and active material mass, resulting in a specific discharge capacity independent of cathode thickness. As the discharge current density is increased, the penetration depth is reduced past the cathode thickness of the thicker cathodes. From here on, the discharge capacity is not proportional to the cathode thickness, and the specific capacity drops. The thinner cathodes follow suit at even higher currents. The utilization of the cathode can be calculated by dividing the specific discharge capacity with the specific discharge capacity at the lowest measured current. Figures 3b and 3d show the utilization (eq. 2) of the cathodes in figures 3a and 3c, respectively, interpolated at a selection of current densities. Here we see the same trend just described. At low current densities the utilization is largely independent of thickness. At higher current densities, the utilization drops sharply at a specific cathode thickness (corresponding to the penetration depth). The thickness at which the utilization drops is reduced as current density is

increase (which is consistent with the behavior of the penetration depth). Overall, figures 3b and 3d share a lot of qualitative similarities to the idealized case shown in figure 2.

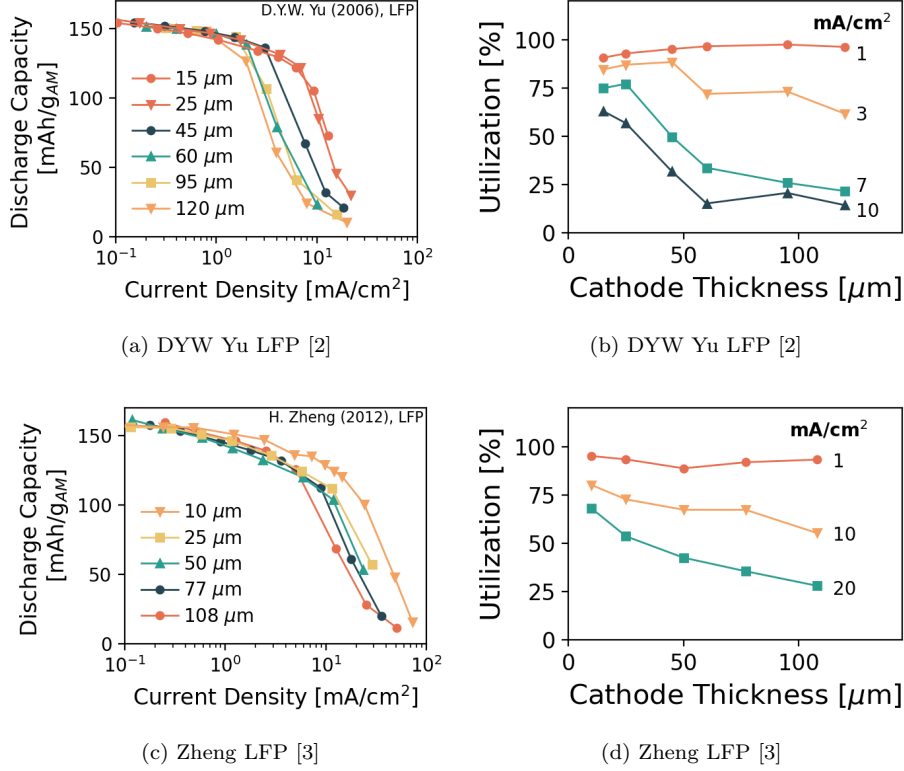
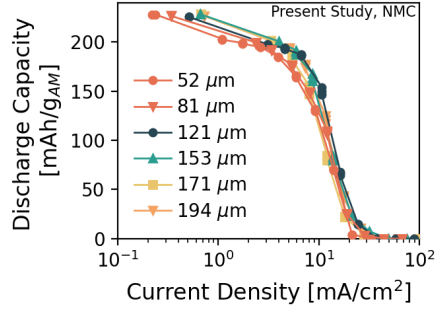


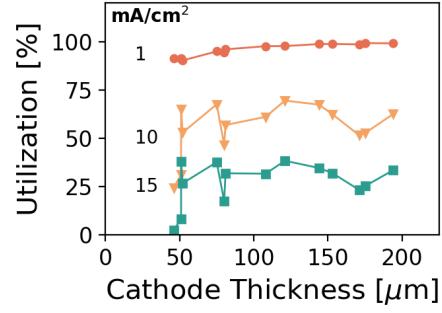
Figure 3: Figures (a) and (c) show the specific discharge capacity for a series of LFP cathodes of different thicknesses, discharged over a range of current densities. The data in (a) and (c) are taken from Ref. [2] and [3], respectively. Figures (b) and (d) show the cathode utilization as a function of cathode thickness, interpolated at a selection of current densities. The utilization drops as a function of cathode thickness. This is an indicator of a diffusion-limited discharge.

The drop at high current densities happens regardless of whether a depletion zone remains at end of discharge, due to limitations in other steps of the discharge. In these cases, you would not expect to see a utilization dependent on the cathode thickness in the same way shown in figure 2. The utilization may have a thickness dependence caused by the various resistances and potentials that are associated with thickness, but not one based on the formation of a depletion zone. In figure 4, shown below, the specific discharge capacity of a series of NMC cathodes with varying cathode thickness, discharged with a series of current densities. The data is taken from the present study (fig. 4a), from H. Zheng’s 2012 study (fig. 4c, [3]), and from C. Heubner’s 2020 study (fig. 4e, [4]). Just like in the case for LFP shown in figure 3, the specific discharge capacity starts high and then drops dramatically around 10 mA/cm². However, in the case of NMC, the specific discharge capacities appear independent of thickness throughout the discharge current range. This is made more clear in figures 4b, 4d, and 4f, where the utilization is plotted against the cathode thickness. The utilization drops as current density is increased, but the drop is largely consistent across all

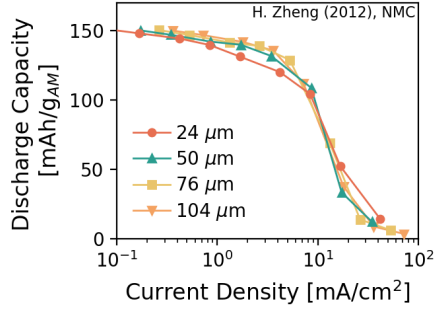
thicknesses.



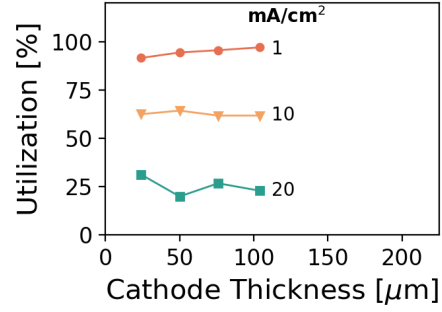
(a) A selection of NMC cathodes from the Present study



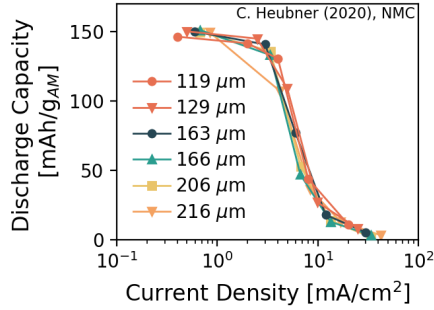
(b) Present study



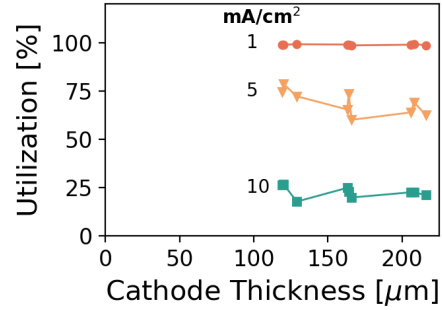
(c) Zheng NMC [3]



(d) Zheng NMC [3]



(e) A selection of NMC cathodes from C. Heubner (2020) [4]



(f) C. Heubner NMC [4]

Figure 4: Figures (a), (c), and (e) show the specific discharge capacity for a series of NMC cathodes of different thicknesses, discharged over a range of current densities. The data in (a) is measured in the present study, while data in (c) and (e) is taken from Ref. [3] and [4], respectively. Figures (b), (d), and (f) show the utilization of the cathodes in figures (a), (c), and (e), respectively, interpolated at a selection of current densities. The utilization is independent of cathode thickness, a sign of a discharge not reaching diffusion limit.

The independence of utilization on cathode thickness means that the depletion zone does not remain at end of discharge in any of them. If it had, you would expect the thicker cathodes to have a larger depletion zone than the thinner ones, and consequently a lower utilization. This raises the question, why does LFP exhibit a thickness effect while NMC doesn't? And what causes the drop in capacity instead?

An important difference between LFP and NMC is that NMC particles are filled as a solid-solution, while LFP particles exhibit a phase-change. This causes the open-circuit potential in NMC to decrease gradually as c_s increases, while for LFP the open-circuit potential has a plateau with near constant potential over a broad c_s range. When an NMC cathode is discharged, the intercalation rate will steadily decrease as the active particles fill up, while with LFP the intercalation rate will be independent of c_s until the active particle is full. Consequently, with NMC the reaction zone is very broad and may stretch across a large portion of the cathode by the time it reaches the current collector, while with LFP the reaction zone will be much more narrow [5]. A larger reaction zone means that there is a larger active surface area participating in the intercalation current. A larger surface area means that the cell current density can be maintained with a lower local current density, a lower overpotential (closer to zero), and a higher applied voltage. Conversely, LFP, with its narrow reaction zone, requires a greater local overpotential (more negative) to maintain the cell current. Consequently, LFP is expected to be more sensitive to a diminishing electrolyte concentration.

This helps to explain why LFP is more likely to exhibit a thickness effect. But it doesn't explain what the mechanism for the capacity drop in NMC is. The drop in capacity must be caused by something that reduces the utilization of the entire cathode. One such example is the solid diffusion in the active particles. The open-circuit voltage is dependent on the lithium concentration *at the surface* of the particle. This means that if the local intercalation rate (per active surface area) into the active particle is faster than the rate of diffusion of the lithium into the center of the active particle, the open-circuit potential at that surface will increase faster. Since the reaction zone stretches across the entire cathode, this solid diffusion limit will impact NMC cathodes of any thickness similarly and end the discharge at a similar level of utilization. Of course, there is still *some* discharge current at which a depletion zone remains at end of discharge, certainly at the current densities where the specific discharge capacity equals zero in the data shown above. But it appears that these depletion zones don't form until after the drop has started. I expect that if one were to discharge NMC cathodes at a high-resolution series of discharge currents from 10 to 20 mA/cm² one would see a thickness effect. If the discharge is limited by the solid diffusion, I would expect the thickness to emerge if the active particles were sufficiently small and sufficiently high nominal capacity.

4 Optimum Thickness

When designing a battery, maximizing the amount of utilized active material relative the amount of inactive materials saves production cost and increases energy density at the cell level. If the cathode is of a material such that discharge is diffusion-limited, the amount of utilized active material is maximized when the cathode thickness equals the penetration depth.

There is an optimum thickness for LFP. But for NMC all we can say is that the optimum thickness is larger than 200 μm , and for any thickness, the current density should not exceed 10mA/cm² or so.

5 Others are making a mistake

All these authors are arguing that the capacity drop in their data (for both LFP and NMC) are caused by a diffusion limit in the electrolyte. My analysis shows that this is not appropriate.

6 Proposal

I make a series of LFP and NMC cathodes of varying thickness and I charge with CCCV them at 0.1 mA/cm², and until they reach a threshold specific capacity, or until they reach a threshold CV current density. Then I discharge them at a series of 10 current densities from 1 to 15 mA/cm², 3 cycles each.

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