INHIBITING THE GROWTH OF LITHIUM DEDRITES BY EMPLOYING
THE ANODIC ALUMINUM OXIDE MEMBRANE

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ABSTRACT

Along with the development of the technology and the increasingly, continuous consumption of the fuel resources. Electrical vehicles seem to be a viable candidate to solve the energy shortage problem. However, the insufficient energy storage impedes the development of the electrical vehicles. The problems of the current lithium ion battery are the low energy density limited by the graphite anode, and the growth of lithium dendrites which utilizes lithium metal as anode will lead to severe safety issues. This thesis aims to improve the performance and the safety of the lithium metal batteries by employing the anodic aluminum oxide membranes (AAO). It is proved that the coin cells with AAO membrane show much better performance than the bare Li – Cu coin cell. It can help the coin cell improve the stability and inhibit the growth of the lithium dendrites. The 20 nm pore size AAO membrane show better performance than that with 35 nm pore size, in which the coin cell with 20 nm AAO membrane can operate over 100 cycles with the columbic efficiency above 90% at 1.0 mA, while the one with 35 nm can only sustain the columbic efficiency above 90% for about 50 cycles. In addition, the symmetric Li – Li coin cell with 20 nm AAO membranes show a much lower overpotential (0.5 V to -0.3 V) than that without AAO membranes (0.05 V to 0.2 V). It means that the lithium is easier to be extracted from under SEI. Therefore, SEI could be more stable and sustain for a longer time, which leads to a stable and high columbic efficiency battery.
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Chapter 1. Introduction

1.1 Motivation of this work

Alone with the development of the modern technology, the energy storage technologies are also required to be advanced. There are numerous types of storage technologies with difference in terms of energy density, power density, product lifetime, efficiency and cost. Among all the technologies, batteries are well developed, manufactured at low cost and commonly utilized in our daily life. The first battery was invented by Count Volta in the 1800s. Batteries such as lead-acid, nickel-cadmium, nickel-metal hydride and lithium ion batteries (LIBs) and others were consecutively introduced. They enabled the development of mobile phone, laptop and more recently electric car; respectively it has changed the way of our communication, working and even transportation. Among them, LIBs have become the most successful energy storage system, which outperform other batteries and occupy 63% of the global market in the whole world.  

Figure 1. (a) The Li-I$_2$ primary Lithium battery; (b) The artificial cardiac pacemaker.
The primary Lithium Metal Battery (LMB) and its advantage—high-energy-density was first introduced by Exxon in the 1970s. It was utilized in small electronic applications such as digital watch, calculators and implantable medical devices. The Li-I₂ primary Lithium battery is still used in cardiac pacemakers. However, the disadvantage is also obvious which is that it cannot be recharged. This would generate high cost, great number of waste and cause environmental pollution.

Then, the Moli Energy developed rechargeable LMB in the late 1980s. The capacity of this rechargeable LMBs is 100 – 200 Wh g\(^{-1}\) or 200 – 300 Wh L\(^{-1}\). However, this rechargeable LMBs also have a severe problem which is the safety issue. The Li dendrites will grow at the Li/ electrolyte interface during the Li plating/ stripping because of its instability. The lithium dendrite would puncture the separator in the battery which causes the short circuit. This leads to a risk of explosion hazards and makes LMB difficult to enter the commercial market. Therefore, strategies against the lithium dendrite growth must be developed.
Figure 3. The scheme of rechargeable Li-ion battery.  

In the 1991, Sony Corporation developed an innovative design of LIBs—LiCoO\textsubscript{2}/C rocking-chair battery, which employed intercalation of lithium ion into the graphite interlayers. This LIB achieved great success because the safety issue of lithium dendrite is solved because lithium is in its ionic state instead of metallic state. For this rechargeable Li-ion battery, the reaction at the cathode is:

\[
\text{LiCoO}_2 \rightleftharpoons \frac{1}{2} \text{Li}^+ + \frac{1}{2} e^- + \text{Li}_{0.5}\text{CoO}_2
\]

Meanwhile, the reaction at the anode is:

\[
\text{C}_6 + \text{Li}^+ + e^- \rightleftharpoons \text{LiC}_6
\]

However, it sacrifices the capacity of battery, since the total capacity of LIB is calculated by:

\[
\frac{1}{\text{Total Capacity}} = \frac{1}{\text{Capacity of Cathode}} + \frac{1}{\text{Capacity of Anode}}
\]

It can be calculated that there is a drastic drop in the capacity of this LIB from 3860 to 372 mAh g\textsuperscript{-1} because of the low capacity of carbon anode. Since the first-generation lead-acid battery was invented, the total capacity has only increased 6-fold from 40 mAh g\textsuperscript{-1} to 240 mAh g\textsuperscript{-1} (the present commercialized LIBs). The growth rates of energy
densities of the batteries have been decelerated, and the energy density of
conventional LIBs have nearly approached the theoretical value of cathodes and
anodes, especially the graphite anode utilized in LIB rechargeable battery as shown in
the figure 3. Therefore, there is an urgent need to find a substitute anode with
remarkable energy density, and lithium is a promising candidate.
1.2 Intrinsic Property of Lithium Metal

The lithium can be the ideal anode for the negative electrode because of its several attracting properties. Lithium is the lightest element in the alkali metal group and has the smallest atomic radius among all the metals, which enables lithium to have a high capacity and quick transfer nature. For the negative electrode, lithium has the most negative potential of all the known electrode materials. This feature provides lithium with a high discharging voltage which leads to a high energy density. The theoretical specific capacity of lithium can be calculated using the following equation:

\[
\text{Specific Capacity} = \frac{\text{charge}}{\text{mass}} = \frac{6.02 \times 10^{23} \text{ atom} \times (1.6 \times 10^{-19} \text{ C atom}^{-1}) \times 1 \text{ mAh} \times 3.6 \text{ C}}{1 \text{ mol} \times 6.94 \text{ g mol}^{-1}} = 3860 \text{ mAh g}^{-1}
\]

Figure 4. Principal and actual energy densities of standard LIBs.  

The lithium ions in the LMBs operate differently from the lithium ions in LIBs. The lithium ions are electrochemically reduced and deposited directly on the lithium metal.
during lithium plating process; and similarly, they are oxidized and stripped away from the lithium metal during lithium stripping process. This hostless nature decides the great capacity of lithium metal. However, such a low potential and high reactivity results in the instability of the lithium metal against electrolyte. It causes several problems which would impede the rechargeable batteries with lithium metal anode from commercialization.
1.3 Challenges against safe and efficient LMBs

1.3.1 Solid Electrolyte Interphase on the Lithium electrode

The first problem is the continuous break and formation of Solid Electrolyte Interphase (SEI). The SEI is the product from the reaction of Li metal and electrolyte at the first cycle. It is consisted of 2 layers near the Li electrode surface and is shown in figure 4 below. The layer closer to the lithium surface is labeled as inorganic layer which contains components such as Li$_2$O, Li$_3$F, LiF, LiOH and Li$_2$CO$_3$. The outer layer is labeled as organic layer and it contains components such as ROCO$_2$Li, ROLi and RCOO$_2$Li while R is the organic group from the electrolyte utilized. It is deducted that firstly the organic layer formed on the lithium metal surface after nucleation, then it transforms into inorganic layer gradually.  

![Figure 5. Schematic structure of the SEI formed on Lithium electrode.](image)
The SEI is electrically insulating and ionically conductive, therefore it can reduce the diffusion resistance of Li ions through this film and help the transportation of Li ions. Therefore, an ideal SEI should also have appropriate thickness which prevents electrons from travelling in the electrolyte but not too thick to impede the diffusion of Li ions. An ideal SEI should also protect the lithium metal anode with high stability. However, because of the extreme volume change of lithium metal anode during repeated Li depositing/stripping processes, the stability of the SEI will be greatly affected. Charles and John \(^6\) investigated the shear modulus of the SEI and its impact on the lithium dendrite growth. It turns out that when the shear modulus of the SEI is around \(10^9\) Pa, Li dendrites can be partially suppressed. However, it was found by Liu et al. \(^7\) and Zhang et al. \(^8\), that the Young’s modulus of the in situ formed SEI film could only achieve 50-400 MPa. Liu and his co-workers researched on the LiF/Li and Li2CO3/Li interface and found out that the mechanical property of the latter one was better. Therefore, more research on artificial SEI film may be one of the viable solutions for the stable SEI film.
1.3.2 Lithium dendrite growth on the Lithium electrode

The second problem is the lithium dendrite growth. In the rechargeable batteries, during the repeating stripping/deposition process, lithium will nucleate and grow on the lithium metal surface. The lithium dendrite growth will cause several problems: the first problem is the safety issue, because of the dendritic morphology, lithium dendrite will penetrate through the separator and reach the cathode, which leads to short-circuit. Then the thermal runaway further leads to the electrolyte combustion and cell explosion. This causes severe safety issues for practical applications of rechargeable Li-anode batteries. The second problem is that the formation of lithium dendrites increases the surface area of lithium electrode. This promotes the parasitic reaction between the lithium electrode and the electrolyte. This irreversible reaction would cause the continuous consumptions of the electrolyte and the conversion of the lithium dendrites to electrochemically inert dead lithium. These will lead a great drop in the columbic efficiency. The lithium metal electrode becomes a porous structure when lithium dendrites grow on it, and this increases polarization and resistance to the ion diffusion. This results in a decrease in the energy efficiency. In addition, the dendrite growth makes the volume change even larger because of the porous lithium deposition.
Figure 6. Schematic images of problems caused by lithium dendrites.  

At present, there are different models which explain this surface nucleation of lithium. One of which suggests two thermodynamic factors for lithium dendrite growth on the electrode surface: lower surface energy and higher migration energy. The combination of these two energies is responsible for the morphology of the dendrite nucleated, lower surface energy leads to one dimensional whiskers. Surface formation energy and diffusion barrier decide whether the uniform deposition can be achieved. In another model—heterogeneous nucleation model, initial stage of the nucleation has a significant effect on the final morphology of the Li dendrites. The heterogeneous nucleation process is divided into five regimes by Ely et al. 10 A nucleation suppress regime, a long incubation time regime, a short incubation time regime, an early growth regime and a late growth regime. In the nucleation suppress regime, the embryos are thermodynamically unstable. Because the nucleus radius does not reach the critical radius, it tends to re-dissolve into the electrolyte. In the long incubation time regime, the thermodynamically favored embryos will grow and the overpotential will increase. When the critical overpotential is exceeded, the lithium embryos are distributed on the electrode surface and the embryos with radius over critical size will grow with the
increasing overpotential. In two growth regimes, the lithium dendrites will grow until they are all the same size. Consider this model, the lithium dendrite growth can be suppressed by the following methods: decrease the roughness of the surface of the lithium metal electrode, improve the wetting of the lithium deposition, limiting the plating overpotential and the size of the anode nucleation site below the critical value. Among these methods, limiting the size of anode nucleation site is tried in this thesis by employing the artificially made AAO (anodic aluminum oxide).

![Image](image_url)

**Figure 7.** a) The SEM image of bottom of the AAO membrane; b) The SEM image of top of the AAO membrane

The AAO is prepared by anodization of highly pure aluminum. It has an advantageous nano-channel structure throughout the membrane. These channels present as a highly ordered hexagonal nano-pore array with even narrow pore size distribution. In addition to its self-ordering ability, AAO also has several other material properties favored for lithium batteries application. For example, it has remarkable wettability which is good for the electrolyte spreading. It also provides with excellent chemical resistance so that it will not react with either electrode or electrolyte. It also has sufficient mechanical strength to suppress the lithium dendrite growth and protect the SEI from the extreme volume change during lithium striping/plating process. The SEM images in the figure 7 show the structure of the prepared AAO in this thesis.
Chapter 2. Experimental

2.1 Preparation of the electrode materials for the battery

Before assembling and testing the coin cells, several materials need to be prepared.

First, the AAO were prepared. The procedures are shown below:

1. Al foil was cut into appropriate size in square shape for later anodization.

2. The 5% oxalic acid solution was prepared and first cooled in the fridge for 30 minutes to around 9 °C.

3. The AAO on the aluminum (AAO@Al) was first prepared by one-step anodization in 5% oxalic acid solution at 40 V for about 4 hours. Two ice blocks were employed beside the apparatus in order to keep the temperature unchanged.

4. Then the alumina was etched away with a mixing acid solution of H₃PO₄ and H₃CrO₄ for at least 12 hours. The Al with an ordered pattern was left.

5. After etching, the Al was again anodized in 5% oxalic acid solution at 40 V for about 2 hours and 20 minutes at 9 °C. Two ice blocks were also employed beside the apparatus in order to keep the temperature unchanged. The thickness of alumina can be adjusted by changing the anodization time.
(6) The prepared AAO@Al had a thickness of around 20 μm and was then coated with PMMA by spin coating. Put the AAO@Al on the spin coating apparatus, vacuum was turned on and PMMA was spread over the AAO. Then the spin speed and the spin acceleration were set to 4000 spins/min and 250 spins/s for 2 minutes. After spin coating, the PMMA on the AAO@Al was dried on the hot plate at 85 °C for 1 minute.
(7) Then the aluminum on the back side was removed by etching in CuCl$_2$. Then it was washed and soaked in deionized water for around half an hour.

(8) Next, the back side of the AAO was etched in the 5% H$_3$PO$_4$ for different time duration for different desired pore-opening sizes, and then washed in the deionized water.

(9) Finally, the PMMA on the AAO was removed by soaked in the acetone. The AAO was ready for the assembly of coin cell after washing and drying. It was put in a small bottle and argon was filled into the bottle.
2.2 Assemble and test of the coin cell

In this thesis, the coin cells were assembled with different anode materials and electrolytes; and tested in the Arbin machine in order to compare the superiority and disadvantage of the AAO@Cu in the Lithium-ion battery. The lab apparatus utilized to assemble the coin cell is the glove box. The operation instructions must be strictly followed for the maintenance of the glove box. After putting the essential items into the chamber, it should be vacuumed, and argon should be filled into the chamber for 3 times. This ensures that no oxygen and moisture go into the glove box. The coin cell consists of 7 parts including two electrode caps (Ni-coated and Sn-coated), one Ni-coated cone spring, one stainless steel spacer, one separator, one Lithium anode and AAO@Cu cathode. There were two electrolytes utilized in the coin cell which were 1M LiPF$_6$ in EC/EMC/DMC (1:1:1, v/v/v) and 1M LiTFSI in DOL/DME (1:1, v/v) with 2% LiNO$_3$. For the Li – Cu coin cell, the self-standing AAO is added between copper foil and separator; and for the Li – Li symmetric coin cell, the self-standing AAO is added between Li and separator.
After the coin cells were assembled, the columbic efficiencies of Li-Cu coin cells and cell lifetime of the Li-Li symmetric coin cells were tested in the Arbin testing machine. The programs were first coded on the computer and then the battery would run following the programs. In this thesis, the Li-Cu coin cells ran at a current of 0.25, 0.5 and 1.0 mA. Therefore, they ran for 4 hours, 2 hours and 1 hour respectively in order to keep the same current density—1 mAh⁻¹. For the Li-Li symmetric coin cell, the test current was set to be 3 mA while the current density was still 1 mAh⁻¹. The impedance of Li-Cu coin cells with and without AAO membrane were also tested from 0.1 Hz to 10⁶ Hz with an amplitude of 5 mV by using the VersaSTAT 4 electrochemical system.
Chapter 3. Results and Discussion

In order to understand the reason why the lithium tends to form dendrites instead of smooth surface growth, understanding the fundamental of lithium dendrite growth is important. Markus et al. 9 carried out research and analysis on the microscopic properties of lithium and explain why lithium tends to form dendrites while magnesium tends to deposit uniformly. Firstly, the basic metallic properties of the lithium metal are discussed. Lithium has a body-centered cubic structure with an eightfold coordination. It has a lattice constant of 3.44 Å and a cohesive energy 1.61 eV/ atom. 10 While Mg has a hexagonal close packed structure with a twelvefold coordination. It has lattice constants of a = 3.19 Å and c = 5.18 Å with a cohesive energy 1.50 eV/ atom. Then the surface energies of both metals are compared. The surface energies of the most stable surface such as (001), (011) and (111) of lithium and (0001) of magnesium are calculated and are summarized in the table. However, their data are similar and therefore, they do not explain the difference between the deposition morphologies of two metals.

Table 1. The surface energies for the most stable surfaces of Li and Mg. 9

<table>
<thead>
<tr>
<th></th>
<th>Li (001)</th>
<th>Li (011)</th>
<th>Li (111)</th>
<th>Mg (0001)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{surf}$/ eV/atom</td>
<td>0.34</td>
<td>0.26</td>
<td>0.54</td>
<td>0.28</td>
</tr>
<tr>
<td>$\gamma$/ J/m$^2$</td>
<td>0.46</td>
<td>0.49</td>
<td>0.53</td>
<td>0.52</td>
</tr>
</tbody>
</table>
Another energy—adsorption energy of two metals—are calculated for the most stable surfaces of two metals: (001) of lithium and (0001) of magnesium. The adsorption energy of the (001) lithium is larger than that of (0001) magnesium. In order to determine how easily it is for adatoms to deposit uniformly, the interaction energies of two metals are also calculated which is simply the difference between the adsorption energies of two isolated adatoms. The possible positions of adatoms on the (4 x 4) surfaces of two metals are shown in the graph.

Figure 11. a) The possible positions of two adatoms on the (4 x 4) surface of Li; b) The possible positions of two adatoms on the (4 x 4) surface of Mg. 

The calculated results are summarized in the table 2. It can be observed that the interaction energies between magnesium adatoms are stronger that that between lithium adatoms. This may because of the lower adsorption energies of magnesium atoms. In addition, the separation between the magnesium adatoms are smaller. These results show that the magnesium atoms tend to form connections with adjacent atoms which results in the uniform deposition; while the lithium atoms tend to stay isolated because of higher interaction energies to be overcome.
Table 2. The interaction energies and the adatom separations of Li and Mg.  

<table>
<thead>
<tr>
<th>2nd adatom site</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li $E_{\text{int}}$/ eV</td>
<td>-0.17</td>
<td>-0.05</td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>Li separation/ Å</td>
<td>3.20</td>
<td>3.91</td>
<td>6.89</td>
<td>7.70</td>
<td>9.74</td>
</tr>
<tr>
<td>Mg $E_{\text{int}}$/ eV</td>
<td>-0.50</td>
<td>0</td>
<td>-0.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg separation/ Å</td>
<td>2.94</td>
<td>6.41</td>
<td>2.95</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In addition to the adsorption and interaction energies, the diffusion barriers also play an important role in the nucleation and growth of the lithium dendrites. Generally, faster diffusion results in a smoother surface and the diffusion mechanism is considered as hopping. Therefore, the diffusion barrier can be calculated by the difference between the adsorption energy of the original atom site and the adsorption energy of the hopping atom site. The results are summarized in table 3. It is clear that magnesium has a much lower diffusion barrier than that of lithium. The diffusion of the lithium atom will be hindered by this high barrier so that it has less tendency to form a uniform deposition on the substrate surface.

Table 3. The diffusion barrier for hopping on Li (001), Li (111) and Mg (0001).  

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{diff}}$/ eV</th>
<th>Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li (001)</td>
<td>0.14</td>
<td>Hopping</td>
</tr>
<tr>
<td>Li (111)</td>
<td>0.41</td>
<td>Hopping</td>
</tr>
<tr>
<td>Mg (0001)</td>
<td>0.02</td>
<td>Hopping</td>
</tr>
</tbody>
</table>
Besides the material properties of lithium metal, it is also important to understand the early stage of the nucleation and growth process of lithium metal. David and his co-worker 11 carried out research on thermodynamic and kinetic aspects of the heterogeneous nucleation and growth of lithium dendrites. Thermodynamically, they calculated the Gibbs free energy of transformation, which is the summation of chemical and electrical energy and the surface tensions:

$$\Delta G_T = \left(\Delta G_f + \frac{\eta \nu F}{V_m}\right) S_V r^3 + \gamma_{NE} S_A r^2 + (\gamma_{SN} - \gamma_{SE}) \pi r^2 \sin^2 \theta$$

Where $\Delta G_f$ is the bulk free energy of transformation, $\gamma_{NE}$ is the surface tension between the nucleus and the electrolyte, $\gamma_{SN}$ is the surface tension between the nucleus and the substrate, $\gamma_{SE}$ is the surface tension between the electrolyte and the substrate, $F$ is the Faraday’s constant, $\nu$ is the valence number of electrodepositing ions $\eta$ is the overpotential and $V_m$ is the molar volume. This decides the stability of the deposition of the nucleus on an electrically charged substrate. The thermodynamic critical radius to form a stable nucleus can be determined when $d\Delta G_T / dr = 0$:

$$r_t^* = -\frac{2\gamma_{NE} V_m}{\eta \nu F + \Delta G_f V_m}$$
Figure 12. The schematic image of a spherical cap-shaped nucleus on an electrically charged substrate in the electrolyte. The volume and the surface area of the nucleus is $S_\text{V} r^3$ and $S_\text{A} r^2$ respectively.\textsuperscript{11}

For the kinetics of electrodeposition, the rate is described by this equation:

$$\Gamma = j_0 \left( \exp \left[ (1 - \alpha) \left( \frac{\eta \nu F}{RT} + \frac{Y_{\text{NE}} V_m \kappa}{RT} \right) \right] - \exp \left[ -\alpha \left( \frac{\eta \nu F}{RT} + \frac{Y_{\text{NE}} V_m \kappa}{RT} \right) \right] \right)$$

Where $j_0$ is the exchange current density, $\alpha$ is the reaction symmetry factor, $R$ is the molar gas constant, $T$ is the absolute temperature and $\kappa$ is the curvature of the substrate surface which means $\kappa$ equals 0 for a flat surface. When the $(\eta \nu F + Y_{\text{NE}} V_m \kappa)/RT << 1$, the equation becomes:

$$\Gamma = j_0 \left( \frac{\eta \nu F + Y_{\text{NE}} V_m \kappa}{RT} \right)$$

For a spherical cap-shaped nucleus, the velocity of growth of nucleus is $v = \frac{dr}{dt} = V_m \Gamma$, and the curvature $\kappa = 2/r$. Therefore, the velocity can be expressed as:

$$v = \frac{dr}{dt} = j_0 V_m \left( \frac{\eta \nu F}{RT} + \frac{2 Y_{\text{NE}} V_m}{r RT} \right)$$
Solve the equation without the applied overpotential:

\[ r(t) = \pm \sqrt{r_0^2 + \frac{4j_0 V_m^2 \gamma_{NE} t}{RT}} \]

This equation reveals that even there is no applied overpotential, it will form lithium dendrite with the time increases. The kinetic critical radius can be obtained by solving \( dr/dt = 0 \) when the Laplace pressure is balanced by the applied overpotential:

\[ r_k^* = -\frac{2 \gamma_{NE} V_m}{\eta v F} \]

Figure 13. Different regimes of the early nucleation and growth of lithium dendrites. \(^{11}\)

In order to obtain the successful nucleation and subsequent growth, the size of lithium embryo needs to exceed both critical radiuses. As summarized in the figure 12, the behaviors of the embryo are divided into four regimes. The blue solid line indicates the thermodynamic stability of the embryos and the black continuous line indicates the kinetic limit of the embryos. The nucleus below the thermodynamic line belongs to
the nucleation suppression regime. This means that the nucleation is not thermodynamically stable and will re-dissolve back into the electrolyte, while the nucleus above the line is energetically favored. Similarly, the nucleus above the kinetic line belongs to the growth regime, which means the nuclei in this area will grow stably; and the nucleus below the line will shrink and finally re-dissolve back into the electrolyte. The area between the thermodynamic line and kinetic line is called incubation regime. The duration of this incubation kinetics depends on the applied overpotential. If the applied overpotential is smaller than \(2\eta_0\), which \(\eta_0\) is the characteristic overpotential and equals to:

\[
\eta_0 = \frac{\Delta G_f V_m}{\nu F}
\]

The nucleus is thermodynamically stable so that it is metastable and will stay in this regime for a long time until it exceeds the kinetic line. Oppositely, if the applied overpotential is greater than the characteristic overpotential, the duration of the incubation regime will be short. At this kind of overpotential, two critical radiuses will be close to each other and leads to favorable local interactions and quick growth. In addition, there is a regime called late growth regime which is not included in this graph. This growth kinetics of this regime is dominated by the localized electric field and the morphology of the nucleus. Therefore, consider these analytical calculations, the lithium dendrite could be suppressed by limiting the anode nucleus size below the thermodynamic critical radius. In this thesis, porous AAO membranes are employed to achieve this.
Figure 14. a, b) The SEM images of 99.9% pure aluminum foil; c, d) The AAO after the first anodization.

By employing the methods described in the experimental section, the AAO with different sizes of pores for the suppression of lithium dendrites can be produced. During the process of making AAO, it begins with a two-step anodization process. This procedure is necessary because the channels in the AAO produced by the first anodization is not straight and therefore there might be an impact on the transportation of the lithium ions. The pores are also not ordered and large enough for the transportation of ions as shown in figure 14. After etching the AAO after the first anodization, it will leave an ordered pattern and will be beneficial for forming an ordered array of hexagonal AAO channels as shown in figure 15.
Figure 15. The SEM images of the ordered pattern on the aluminum foil after 12 hours etching in a mixing acid of 3% H₃PO₄ and 3% H₃CrO₄.

This aluminum with an ordered pattern is again anodized for 2 hours and 20 minutes to obtain a desired thickness of AAO. Because the AAO channels grow from this ordered pattern. As shown in figure 16, the channels are also forming a hexagonal array and straight which would be beneficial for the transportation of the lithium ions.

Figure 16. The SEM images of AAO after second anodization: a, b) The 2nd anodization AAO without etching; c, d) side view of the AAO channels.
Figure 17. The SEM images of the back side of the AAO membranes: a-b) no opened-pores after 90 minutes etching; c-d) 20 nm pores after 92 minutes etching; e-f) 35 nm pores after 100 minutes etching.

In another step that the back side of the AAO is etched by the 5% phosphoric acid, the etching time can be adjusted to 92 and 100 minutes, which the sizes of the pores at the back side will be around 20 and 35 nm respectively. The SEM images of these AAO membranes are shown in figure 17.
To examine the reversibility of the lithium deposition process, the columbic efficiency, as an indicator, of the coin cells without and with different pore sizes of AAO membranes are determined. It is obtained by cycling the lithium metal anode against the copper current collector. A fixed current density is set to ensure the same amount of lithium are stripped and deposited each cycle. Then the columbic efficiency can be calculated by determining the recoverable charge as a percentage of the discharge capacity.

![Figure 18](image)

Figure 18. The comparison of the columbic efficiencies of coin cells with different electrolytes—LiPF₆ and LiTFSI

Firstly, the coin cells assembled with different electrolytes—LiPF₆ and LiTFSI are examined. As shown in the figure 18, it is obvious that the performance of the coin cell with LiTFSI is much better and more stable than the one with LiPF₆. The first reason is that LiPF₆ is carbonate-based electrolyte which is highly corrosive. The second reason
is that the exchange current density of carbonate-based electrolyte LiPF$_6$ (35 mA/cm$^2$) is higher than that of the ether-based electrolyte LiTFSI (25 mA/cm$^2$) with the additives of LiNO$_3$ and Li$_2$S$_8$. These two additives act as strong inhibitors molecules and the lower current density leads to the growth of the lithium dendrites with compactly packed round morphology. Compared to commonly formed lithium dendrites—randomly oriented whiskers, this packed round morphology will reduce the surface area of lithium dendrites and result in less formation of SEI. This will lead to less consumption of lithium and electrolyte, and therefore increase the columbic efficiency of the coin cell.

Figure 19. The test results of the columbic efficiency of three different coin cells: a) Li – Cu without AAO membranes; b) Li – Cu with 35 nm AAO membranes; c) Li – Cu with 25 nm AAO membranes; d) The comparison of the columbic efficiencies of three different coin cells.
Then, the coin cells are all assembled with the electrolyte LiTFSI. One kind is without the AAO membrane, and the other two kinds are assembled with 20 nm and 35 nm AAO membranes. The columbic efficiencies of these coin cells are collected and presented in the figure 19. It can be seen that the columbic efficiencies of their first cycle are all low. It may because of the formation of the SEI during the first cycle, and this consumes the lithium and electrolyte, which leads to a low columbic efficiency. From 19a, b and c, it can be observed that the performance of the coin cells will be greatly influenced by the magnitude of the current. At large current, except the coin cell with 20 nm AAO membranes, it is difficult to sustain a high columbic efficiency above 90% for more than 100 cycles. It is because that a large current will cause severe dendrite growth; while at a small current, the lithium can deposit more uniformly. Therefore, the columbic efficiencies of three different kinds of coin cells do not have much difference at small current (0.25 mA). However, as the current increases to 0.5 and 1.0 mA, the coin cell with 20 nm AAO membranes becomes the best among all the coin cells. As it can operate stably with a high columbic efficiency above 90%; while the coin cell without AAO membrane can only sustain the columbic efficiency above 90% for around 30 cycles, and the coin cell with 35 nm can sustain the columbic efficiency above 90% for around 50 cycles. The columbic efficiencies of three different coin cells at 1.0 mA are compared in figure 19d, and the AAO membranes with smaller pore size will greatly improve the performance of the coin cells.
In order to investigate the effect of the AAO membranes, two coin cells are made for test. One is bare Li-Cu coin cell without AAO membranes and the other one is added with AAO membranes which has 20 nm pores at the back side. Then they run for 10 cycles at 0.5 mA. The coin cells are dismantled, and the copper plates are taken out.

The SEM images of these two copper plates are shown in figure 20. It is clear that the deposition of lithium is more uniform on the copper plate in the coin cell with AAO membranes than that without AAO membranes. The lithium tends to form dendrites even though some of them has a sphere like morphology.
The experiment results of Li-Li symmetric coin cell at a current of 5.0 mA and a current density of 1mA/h with the electrolyte of LiTFSI: a) without AAO; b) with the addition of AAO with 20 nm pores between both lithium metal plates and separator.

The galvanostatic lithium cycling experiments were also performed in which the lithium is continuously plated and stripped in Li-Li symmetric coin cells. The experiments were performed at a fixed current of 5 mA and a fixed current density of 1 mA/h. The difference between the tested coin cells is that one is made with the addition of AAO membranes which has 20 nm etched pores at the back side between both lithium metal plates and the separator. The voltage profiles of the symmetric coin cells are shown in the figure 21. It can be observed that the overpotential of the symmetric coin cells increases clearly at the end of either charge or discharge of that cycle. This reflects how easily the lithium can be stripped from the metal plate which is covered by a layer of SEI. Although both coin cells ran over 1000 cycles, the overpotential of the symmetric coin cell without AAO membranes (from 0.5 V to -0.3
V) is much larger than that with AAO membranes (from 0.05 V to 0.2 V). This represents that the cell can stably operate for a longer time since the SEI would be more stable and sustain for a longer time.

![Figure 22](image.png)

*Figure 22. The measured impedance of the coin cells with and without AAO membranes.*

Although the AAO membrane with 20 nm pore at the back side improve the performance of the coin cell, it also brings the concern, as the AAO membrane is an electrical insulator, whether the AAO membrane will influence the ohmic resistance of the battery. Therefore, the impedance of all the coin cells with different configurations are measured. By employing the circular fit function on the software VersaStudio, the ohmic resistance of the coin cell can be determined. For the bare Li – Cu coin cell, and the coin cells with the AAO membranes which have 20 nm and 35 nm pores at the
back side, their impedance are 772.2 Ω, 714.1 Ω and 817.7 Ω. The impedance of these coin cells is close to each other, which also can be seen from figure 22. This could prove that the addition of the AAO membranes with pores opened at the back side can greatly improve the performance and the stability of the battery, while have nearly no effect on the ohmic resistance of the whole coin cell.
Chapter 4. Conclusion and Future Outlook

This thesis investigated the present challenges for the development of the lithium metal batteries—the growth of the lithium dendrite and the instability of the SEI, and how to inhibit the growth of the lithium dendrites is focused. Consider the model that the size of the lithium embryo must exceed the critical radius to become both thermodynamically and kinetically stable before it grows into lithium dendrites. Therefore, the anodic aluminum oxide membrane with different sizes of pores opened at the back side is prepared to suppress the lithium dendrite growth by limiting the size of the embryos.

From the columbic efficiency of the Li – Cu coin cell, the overpotential of the Li – Li symmetric coin cell and the impedance of the Li – Cu coin cell, it is proved that the AAO membrane can greatly improve the performance and the stability of the battery, especially at a large current. The SEM images of the copper plate cathode also prove that the AAO membranes can greatly suppress the lithium dendrite. While the addition of the AAO membrane does affect the ohmic resistance of the coin cell itself. It is also found out that smaller pore size can provide with a better performance and stability. Therefore, it is worth trying to test the electrochemical performance of the coin cell with larger or smaller pores to find out exact relation between the pore size and the performance of the battery. In addition, since the function of the AAO membrane is more useful and obvious at a large current, its performance in the full cell in which the anode is lithium metal is also expected.
Reference


