

Joakim Hirsch

Choice of Liquid Electrolytes In Anode Free Lithium Metal Batteries and its Impact on Lithium Morphology

Bachelor's thesis in Chemistry
Supervisor: Øystein Gullbrekken
April 2022

Joakim Hirsch

Choice of Liquid Electrolytes In Anode Free Lithium Metal Batteries and its Impact on Lithium Morphology

Bachelor's thesis in Chemistry
Supervisor: Øystein Gullbrekken
April 2022

Norwegian University of Science and Technology
Faculty of Natural Sciences
Department of Chemistry

Abstract

An increase in demand for energy dense batteries coming from electric vehicle has created an incentive to develop new technology for energy dense electricity storage. One technology that has the possibility to fulfill these demands is anode free lithium metal batteries (AFLMBs). The lack of an initial anode material gives AFLMBs an increased energy density over lithium ion batteries, but also results in AFLMBs having low cycle life alongside some safety concerns. In this thesis the current strategies and challenges of AFLMBs are discussed, with a focus on the choice of electrolyte. The use of ether based solvents with a high dual lithium salt concentration were found to give the best performance. The cycle life and safety of the battery remains too poor for practical applications, even with the optimized electrolyte. AFLMBs show great promise and may show widespread adoption in the future, but more research into stabilizing the deposited lithium's morphology is needed to see this adoption.

Contents

1	Introduction	1
2	Theory	1
2.1	Lithium ion batteries	1
2.2	Lithium metal batteries and anode free lithium batteries	3
3	Discussion	5
4	Conclusion	11

1 Introduction

The need for efficient and sustainable energy storage is increasing with the shift towards more environmentally friendly transportation^[1]. The transition towards more electric vehicles has produced a greater incentive to create batteries with a higher energy density^[2]. One of the possible technologies that could underpin the efforts to move to electric transportation are anode free lithium metal batteries (AFLMBs). These batteries have a substantially greater energy density than the lithium ion batteries (LIBs) that are state of the art today^[3;4]. Even though LIBs are the most energy dense batteries in commercial use today a more energy dense battery is advantageous in application such as electric vehicles and electric aviation.

The two greatest problem hindering the adoption of AFLMB today is their low cycle life and safety^[5;6;7]. The low cycle life of the batteries are a consequence of the anode free design. The lack of an anode material for the lithium ions to intercalate into results in the lithium being plated directly onto the anode current collector as lithium metal. The relatively low reversibility of this plating/stripping is the cause of the low cycle life^[5;6;7]. The safety concerns are also a result of the plating of lithium metal. The possibility of lithium dendrites short circuiting the battery and causing thermal runaway or in worst the case combustion^[6].

The design of the electrolyte is regarded as one of the most promising modes of improving the cyclability of AFLMBs^[8], as such the focus of this thesis will be on design/choice of electrolyte in AFLMBs and the impact this has on the lithium morphology and resulting cycle life. The cycle life and energy density of AFLMBs and LIBs will be compared and the potential future use of AFLMBs will be discussed.

2 Theory

2.1 Lithium ion batteries

Lithium ion batteries (LIBs) are energy storage devices that stores electrical energy by using the difference in electrochemical potential between two electrode materials where lithium is reversibly oxidized and reduced.

A conventional lithium ion battery (LIB) consists of seven parts: The cathode current collector, the cathode material, a separator, the anode material, the anode current collector, the electrolyte, and a containment material^[4]. During discharge, energy is released from the battery in the form of electrons flowing from the anode (negative electrode, negative [-] terminal) to the cathode (positive electrode, positive [+] terminal) through the current collectors and an external circuit. The names of the electrodes are assigned during discharge even though their function changes during charging. An oxidation reaction is taking place at the anode during discharge, and a reduction reaction is taking place at the cathode. At the same time and rate of electrons flowing though the circuit there are lithium ions also moving from the anode to the cathode through the electrolyte. The energy that is released as electrical energy stems from the potential difference of lithium ions intercalated in the anode and the cathode. Lithium in the anode has a higher potential than lithium in the cathode. If an external electrical potential greater than the potential difference of the battery is applied then the movement of electrons

and lithium ions is reversed and the battery is charged.

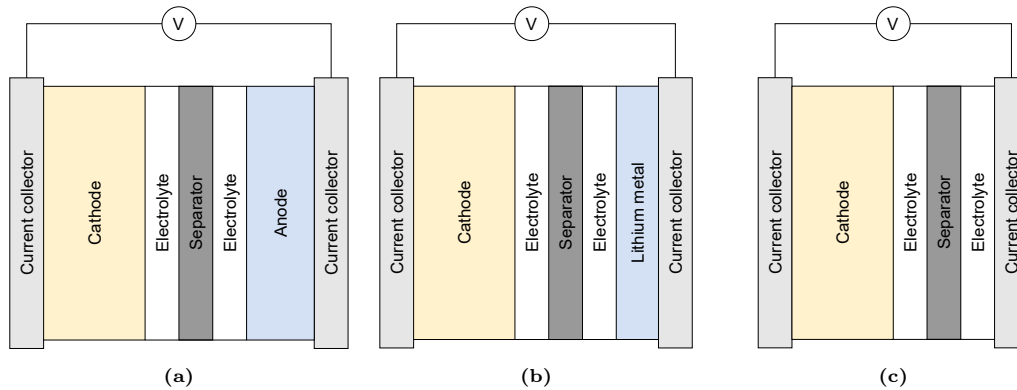


Figure 1: (a): The general structure of a lithium ion battery. (b): The general structure of a lithium metal battery. (c): The general structure of an anode free lithium metal battery.

As mentioned previously the function of the cathode is to be a lithium ion acceptor during discharge and a lithium ion source during charging. For this purpose cathode materials used in LIBs are lithium containing inorganic materials, most commonly lithium iron phosphate (LiFePO_4), lithium cobalt oxide (LiCoO_2) or lithium nickel manganese cobalt oxide (NMC)^[9]. Several different compositions of NMC has been used in batteries. To denote different compositions the ratio of nickel, manganese and cobalt is given after NMC. As an example $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}]\text{O}_2$ is abbreviated as NMC532.

The anode functions as a Li^+ source during discharge and a Li^+ acceptor during charging. The most commonly used anode material in LIBs is graphite^[4]. The mechanism of lithium exchange is intercalation. Intercalation is the reversible insertion of a ion/atom/molecule in between the layers of a layered structure. Both electrodes should have a high degree of reversibility in lithium intercalation/deintercalation and high chemical, electrochemical and thermal stability.

The current collector is used to extract electrical current from the anode, and the cathode and guide it to the external circuit the battery is powering^[4]. This function is relatively simple but essential. For a current collector to function properly it needs to have a high electronic conductivity. The stability of the current collector is also of great importance. It must be chemically and electronically stable against corrosion and parasitic reaction, but also it must have sufficient mechanical strength to withstand the pressure exerted on it from the volume changes during cycling. The thermal stability of the material is also important. A high thermal stability facilitates a wider range of operating temperatures^[7]. Materials that have these characteristics are typically transition metals. The cathode current collector is most often made of aluminum (Al) and the anode current collector is made of copper (Cu)^[4].

Between the cathode and the anode there is a separator. The separator acts as a semipermeable insulator between the anode and the cathode. Its function is to inhibit current flow directly between the cathode and the anode, and forcing all the current through the current collectors therefore inhibiting short circuiting, but to still allow for ionic conduction between the electrodes. The important characteristics of a separator is its permeability, porosity, electrolyte absorption/retention and its chemical, mechanical and thermal stability^[10]. Separators are most often polymer based materials. The most used polymers are polyethylene (PE), polypropylene

(PP), polyethylene oxide (PEO), Polyacrylonitrile (PAN), polymethyl methacrylate (PMMA) and Polyvinylidene fluoride (PVDF)^[10].

For the battery to function there must be lithium ion transport between the electrodes. A solution of lithium salts dissolved in organic solvents are used to facilitate this transport. Electrolytes for LIBs are hard to optimize since they are a compromise between several properties where the lack of a single one can drastically reduce the electrolyte's performance and therefore the batteries performance. The important properties of a electrolyte is: electrochemical, chemical and thermal stability, low electrical conductivity, high ionic conductivity, great wettability of electrodes, and separator and formation of thin and stable solid electrolyte interphase (SEI)^[7]. A description of what a SEI is and its function and properties is found below.

The electrolyte in LIBs is most often an organic solvent with dissolved lithium salts and possibly additives. The most commonly used solvents are either linear or cyclic organic carbonate. Common linear carbonates are dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC)^[4]. Common cyclic carbonates are ethylene carbonate (EC) and propylene carbonate (PC)^[4]. These solvents are chosen for their electrochemical stability, low cost and their favorable compatibility with intercalation electrodes^[7]. EC specifically is chosen for its ability to readily dissolve lithium salts. Other (often linear) solvents are often added to reduce the viscosity of EC, and to help increase the ionic conductivity.

The most commonly used lithium salt is lithium hexafluorophosphate (LiPF_6), but other salts are also used, such as: lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), lithium bis(fluorosulfonyl)imide (LiFSI), lithium bis(oxalato)borate (LiBOB) and lithium difluoro(oxalato)borate (LiDFOB)^[4]. These salts are selected for their great solubility in the solvents, their high electrochemical stability, high ionic conductivity and their interaction with and formation of favourable SEI.^[7] Additives are also used in electrolytes. The most used additives are vinylene carbonate (VC) and fluoroethylene carbonate (FEC). Additives are often added to improve the formation of a favourable SEI during the initial cycles of a battery. After the formation of a SEI the additives have less favourable characteristics than other solvents, so the concentration of the additives is often just large enough to create the SEI.

During cycling, electrolyte in contact with the electrode will form a solid layer of decomposed electrolyte components in the interphase between the electrolyte and the electrode^[11]. This solid electrolyte interphase (SEI) comes from electrolyte components that are not stable at the high/low potentials of the electrodes and decompose and deposit on the surface of the electrode. The properties of this interphase has a great impact on the performance of the battery. The SEI passivates the electrodes therefore hindering further electrolyte decomposition. An ideal SEI has low electron conductivity, high Li^+ conductivity and high electrochemical, chemical and thermal stability^[11]. A large portion of the SEI formed during the entire life of the battery is formed during the initial cycles of the battery when the electrodes are in direct contact with the electrolyte. This results in the battery having a low CE during the initial cycles.

2.2 Lithium metal batteries and anode free lithium batteries

The principle structural change from a lithium ion battery (LIB) to a lithium metal battery (LMB) is the use of metallic lithium as a anode material instead of graphite, as can be seen

in the structure of the battery given in figure 1b. Lithium metal is an ideal anode material due to its very low electrode potential (-3.04 V vs standard hydrogen electrode) and low density (0.543 g cm^{-3})^[12]. Li's low density also results in it having a very high specific capacity (3820 mAh g^{-1})^[12]. These properties gives a LMB a greater energy density than a LIB. Another change is in the charge/discharge mechanism of the anode. During charging of a lithium ion battery lithium ions are intercalated into the anode material, and deintercalated during discharging. In a lithium metal battery the lithium ions are plated onto the lithium anode, and are stripped off the anode into the electrolyte during discharging.

Lithium metal batteries have some challenges. The main challenges are safety, cycle life and cost^[5;6;7]. Metallic lithium at the anode reacts violently in contact with the moisture in the air in case of a battery puncture or moisture in the electrolyte. The lithium foil that is used as the anode material is also expensive to produce and expensive/difficult to handle in production of the batteries^[6]. Some fraction of the metal at the anode in a LMB is also redundant. This excess lithium, lithium metal at the anode that does not take part in the electrochemical process of the battery, is extra weight and volume that is not necessary for the function of the battery. A reduction in the amount of excess lithium increases the energy density of the battery^[5;7]. This increase continues until there is no lithium at the anode at all when the battery is fully discharged. This means all the lithium used in the cycling of the cell comes from the cathode. This design is called an anode free lithium metal battery^[13].

The structure of an AFLMB is given in Figure 1c. These anode free lithium metal batteries (AFLMBs) functions quite similarly to a LMB during regular cycling, the difference is in the start of charging and end of discharging. At the start of charging lithium is deposited onto the copper current collector instead of onto the lithium anode as in LMBs, likewise during the end of discharging where lithium is stripped off this current collector instead of off the lithium anode^[6]. During the rest of the cycle when there is a substantial layer of lithium on the current collector the AFLMB functions identically to a LMB. As a consequence of not having excess lithium metal at the anode, AFLMBs have higher volumetric and gravimetric energy density^[14]. Potentially the biggest problem limiting the use of AFLMBs is their poor cycle life^[5;6;7;14].

Since all the lithium used in the charging/discharging process is originally from the cathode, any lithium that is not reversibly plated onto the current collector is no longer available to be used in cycling thus reducing the capacity of the battery^[15]. The two most important mechanisms that cause lithium to no longer be available to the battery is: SEI growth and creation of "dead" lithium. SEI formation consumes the electrolyte. Dead lithium is metallic lithium that is no longer has an electrical connection to the anode current connector and does therefore not take part in the battery cycling^[16].

A method for quantifying the loss of available lithium is coulombic efficiency (CE). Coulombic efficiency is defined in this application as the ratio between lithium ions that are stripped from the current collector during discharge and the number of lithium ions that are deposited onto the current collector during charging^[15]. The relationship is given in equation 1. A battery should be replaced when its capacity drops under 80% of its original capacity^[17]. From this and the coulombic efficiency of the battery an estimate of the cycle life of the battery can be

calculated^[15]. A selection of cycle lives and the average CE that is required to reach this cycle life is given in Table 1. From this table it can also be observed that a CE very close to 100% is needed to reach a long cycle life.

$$CE = \frac{\text{Number of Li}^+ \text{ ions stripped}}{\text{Number of Li}^+ \text{ ions deposited}} = \frac{\text{Discharge capacity}}{\text{Charge capacity}} \quad (1)$$

Table 1: Theoretically required coulombic efficiency (given in percent) for a battery for a number of cycles, given that the battery retains 80% of its starting capacity at the specified number of cycles.

Number of cycles	Required CE
50	99.55%
100	99.78%
200	99.89%
500	99.96%
1000	99.98%

3 Discussion

The main benefit of AFLMBs over LIBs are their increase in theoretical energy density. The theoretical specific capacity of lithium metal as an anode is 3862 mAh g^{-1} compared to the much lower capacity of the graphite anode: 372 mAh g^{-1} ^[6]. This increase in theoretical specific capacity of the anode gives the battery as a whole greater theoretical energy density. Louli et al. compared an anode free lithium metal battery with a lithium ion battery. Both batteries used and identical NMC ($\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}]\text{O}_2$) cathodes. The LIB had an synthetic graphite anode, while the AFLMB had no anode. The AFLMB had an 80% increase in volumetric energy density and 54% increase in specific energy density compared to the LIB^[18]. Even though AFLMBs have a energy density advantage over LIBs they have yet to be used in practical applications, and have yet to be commercialised. This in mainly because of safety issues and the previously mentioned poor cycle life^[5;6;7].

One of the obstacles that hinders homogeneous lithium deposition is the mismatch in lattice structures between Li and Cu (*bcc* (110) for Li and *fcc* (111) for Cu).^[16;19] Li also has a large nucleation overpotential/nucleation energy against Cu. This mismatch results in Li not being able to wet the surface of the Cu current collector leading to inhomogeneous lithium deposition^[16]. Another obstacle is the mass transport of Li^+ from the bulk electrolyte to the surface of the current collector, their adsorption and reduction, and the surface diffusion before the ions are incorporated into the lattice^[20]. During the charging process, Li^+ is deposited onto the current collector from the electrolyte, reducing the concentration of Li^+ at the surface of the deposited lithium. This reduction in Li^+ concentration and unavoidable convection can cause a concentration gradient of Li^+ to form in the electrolyte^[20]. The deposition rate of Li is dependent on the concentration at the surface. If an inhomogeneous lithium deposition appears at the current collector its outer part is in a higher concentration than its inner parts. This is shown in Figure 2. This causes a cascade where the now dendritic formation grows further into the electrolyte which further increases the concentration which again accelerates the growth of the dendrite^[20]. Another cause of this formation is the low surface mobility/migration of de-

posited Li. This low surface mobility/migration causes inhomogeneous deposition to propagate instead of terminate^[19].

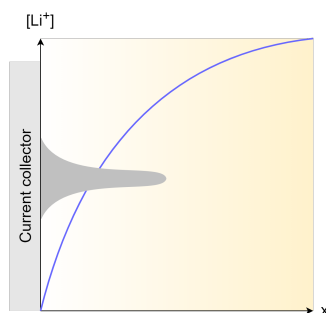


Figure 2: A visualization of the concentration gradient of Li^+ close to the deposited lithium, and a lithium dendrite growing out into the more concentrated electrolyte.

The formation of dendrites and inhomogeneous morphology is the main cause of the low CE of AFLMBs. The formation of dendrites and "mossy" lithium morphology results in a large surface to mass ratio. Since the formation of SEI happens at the surface of the deposited lithium a high surface to mass ratio will cause increased formation of SEI. This will consume more of the electrolyte and more of the available lithium. The inhomogeneous SEI does also contribute to further inhomogeneity in future lithium deposition. A inhomogeneous SEI will cause inhomogeneous ionic conduction since the thickness of the SEI is changing.^[7]

Several possible methods to suppress the formation of dendrites and inhomogeneous deposition have been proposed. These methods (except for liquid electrolyte design) are not the focus of this thesis, but should be mentioned for perspective. One method of improving Li morphology is the application of mechanical pressure. Louli et al. found that an increase in initial average pressure exerted onto the cell from 75 kPa to 2205 kPa was generally beneficial to the plating efficiency in AFLMBs^[21]. Another possible solution to the cycle life problem is the use of a specially designed current collector. There are multiple possible ways to improve the current collector. Using a wetting agent, such as Au, Ag, Pt, Zn, Al, Mg, Si, Sn, and C, can improve the Li morphology by reducing the nucleation overpotential^[16]. The use of 3D porous Cu/C/Ni electrodes has also shown promise^[16]. Another but less practical method is the specially designed cycling protocols. A slow charge rate and a fast discharge rate has been found to increase cycling stability^[7]. This is impractical since the most common uses of batteries, such as in electric vehicles and mobile electric devices, benefit from a fast charge and slow discharge rates. Solid electrolytes has potential to improve AFLMBs owing to their good mechanical strength, low flammability, chemical/electrochemical/thermal stability, possibility for high Li^+ conductivity and high Li^+ transport numbers^[7].

The choice of solvent is a big factor in determining the ionic conductivity, viscosity, wettability of the electrolyte, and has a big impact on the structure and composition of the SEI. Both carbonate based electrolytes and ether based electrolytes have shown good results in AFLMBs^[12;22;8;3]. Traditional carbonate based electrolytes, such as EC/DEC, have shown good results without additives or novel salt selections. Sahalie et al. found that a AFLMB (Cu || NMC111) with a 1 M LiPF_6 EC/DEC 1:1 v/v electrolyte only retained $\approx 40\%$ capacity after 15 cycles^[23]. The battery performed better with potassium nitrate KNO_3 as an additive,

retaining $\approx 40\%$ capacity after 50 cycles^[23]. The low cycle life of the battery without the additive is a result of poor lithium morphology^[23]. The increase in performance in the KNO_3 containing battery is a result of the synergistic effects of the K^+ and NO_3^- ions. The NO_3^- ion is reduced and creates a SEI consisting of a high portion of inorganic components (Li_3N , Li_2O , LiN_xO_y , and LiF) giving the SEI higher ionic conductivity, while the K^+ ions exert electrostatic shielding on the outer parts of dendrites, slowing their growth^[23].

Several studies suggests ether based solvent shows good compatibility with AFLMBs^[8;12;24]. Qian et al. found a large improvement in the cycle life of a AFLMB in replacing a conventional carbonate electrolyte (1 M LiPF_6 - EC/DMC 1/2 v/v) with an ether based solvent (4 M LiFSI - 1,2-dimethoxyethane (DME)). An increase in the CE of the initial cycle from $\approx 25\%$ to 96.6%^[24]. The reversibility of the DME battery remains good during the entire cycle life of the battery, reaching an average CE of greater than 99%^[24]. It was found through x-ray diffraction that the DME SEI consisted of a significant amount of lithium containing inorganic materials.^[24] The group argued that the appearance of significant lithium containing inorganic components in the SEI enhances its ionic conductivity and lengthens the battery's cycle life^[24].

One other possible solution to the challenges of solvent choice is solvent molecule tuning. Yu et al. found that a family of ether based fluorinated-1,2-diethoxyethane (fluorinated-DEE) gave AFLMBs with high CE and cycle life^[8]. Through analysis of several variants of fluorinated-DEE it was found that the (F4DEE) and (F5DEE) gave a very high CE and quick stabilization of CE from first charge^[8]. An anode free battery with a microparticle-LFP cathode ($\sim 2.1 \text{ mAh g}^{-1}$) with a 1.2 M $\text{LiFSI}/\text{F5DEE}$ electrolyte retained 80% capacity for greater than 140 cycles^[8]. A homogeneous and flat lithium morphology was observed in all the fluorinated-DEE solvents, but the batteries using F4DEE and F5DEE showed a slightly better morphology^[8]. The group claimed that the increased performance the fluorinated solvents presents was a result of greater proportion of LiF in the SEI. Yu et al. also claimed that the poorer performance of F3DEE and F6DEE compared to the F4DEE and F5DEE came SO_xF species remained at the top surface of the Li metal in the F3DEE and F6DEE cells. The presence of SO_xF indicates incomplete anion decomposition^[8]. A complete anion decomposition can results in a higher proportion of ionically conductive species, such as LiF or Li_2O , in the SEI. These results indicates that a high proportion of inorganic species in the SEI is advantageous in formation of a homogeneous lithium deposition.

One commonality in the previous studies is how the composition of the SEI impacts CE. A high portion of inorganic species is tied to good reversibility. This is also supported by the study performed by Jurng et al. Their study focused on how the electrolyte influences the nanostructure of the SEI, and its influence in the battery's performance. They found that a homogeneous nanostructure of LiF particles leads to a uniform diffusion field gradient that leads to a uniform deposition of lithium on the current collector^[25].

A lot of interesting research has recently been done on different lithium salts in AFLMB electrolytes. The effect different lithium salts has on SEI formation, lithium morphology an performance of the battery has been studied. Beyene et al. compared AFLMB three cells ($\text{Cu}||\text{LFP}$) using the same solvent (DME/1,3-dioxolane (DOL) 1:1 v/v) with three different salt combinations: 3 M LiTFSI (3TFSI), 2 M LiFSI + 1 M LiTFSI (2FSI+1TFSI), and 1 M

LiFSI + 2 M LiTFSI (1FSI+2TFSI). It was found that the (2FSI+1TFSI) outperformed the other electrolytes, reaching a CE of 98.8% after 100 cycles^[12]. This increased performance came from the synergistic effects of LiFSI and LiTFSI^[12]. LiFSI is reduced earlier than LiTFSI and results in a thin, strong SEI that is rich in ion conduction inorganic species (LiF, Li₂O and Li₂CO₃), while LiTFSI remains in the electrolyte and keeps the ionic conductivity of the electrolyte high^[12]. This was confirmed with scanning electron microscopy of the deposited lithium, where the morphology of (2FSI+1TFSI) was observed to be more uniform and flatter than for the other electrolytes^[12]. The lithium morphology of the (1FSI+2TFSI) electrolyte was more uniform than that for (3TFSI) reinforcing that the increase in performance came from the reduction of LiFSI^[12]. The importance of a thin and strong SEI is again demonstrated. The observation of a SEI with a high content of inorganic components improving the performance of the battery is also in agreement with previously mentioned studies. This also indicates that it is possible to select different salts for SEI formation and ion transport, instead of optimizing one salt for both tasks.

Another group that investigated the effects of dual salt electrolytes was Weber et al. They compared a range of salts and salt combinations in a carbonate based (fluoroethylene carbonate (FEC):DEC 1:2 v/v) electrolyte^[22]. The single salt electrolytes (1 M LiPF₆ and 1 M LiBF₄) showed poor cyclability, falling under 80% capacity retention within 15 cycles^[22]. The single salt electrolyte using 0.6 M and 1 M LiDFOB showed greater performance, dropping under 80% capacity retention within 50 and 60 cycles respectively^[22]. The best performing electrolytes were the dual salt electrolytes consisting of LiDFOB and LiBF₄. Two different concentrations of this electrolyte was tested: 0.6 M LiDFOB + 0.6 M LiBF₄ and 1 M LiDFOB + 0.2 M LiBF₄ reaching 80 and 90 cycles before dropping under 80% respectively^[22]. One interesting result was observed with an electrolyte containing 0.6 M LiDFOB and 0.6 M LiPF₆. This electrolyte showed no improvement over 0.6 M LiDFOB^[22], indicating that there are no synergistic effects between the two salts. The SEI of cells containing salts LiDFOB + LiBF₄ were found to contain significant amounts of both organic and inorganic fluorine components^[22]. This shows both agreement and disagreement with the previously mentioned studies. The best performing batteries contained a significant amount of inorganic fluorine. But there were also cells with a higher proportion of inorganic fluorine that had a shorter cycle life than the LiDFOB + LiBF₄ cells. This indicates that there may be an optimal proportion of organic and inorganic components that forms an ideal SEI.

A followup study performed by the same group was performed. Louli et al. found that a 0.6 M LiDFOB + 0.6 M LiBF₄ FEC:DEC 1:2 v/v electrolyte performed better than the conventional 1 M LiPF₆ EC:DEC electrolyte^[3]. They also found that a more concentrated electrolyte (2 M LiDFOB + 1.4 M LiBF₄ FEC:DEC 1:2 v/v) resulted in longer cycle life than a less concentrated electrolyte 0.6 M LiDFOB + 0.6 M LiBF₄ FEC:DEC 1:2 v/v^[3]. A high concentration electrolyte battery also retained greater energy density than a LIB with the same cathode (Li[Ni_{0.5}Mn_{0.3}Co_{0.2}]O₂ (NMC532) | graphite, 1.2 M LiPF₆ EC:EMC + 2% VC + 1% 1,3,2-dioxathiolane 2,2-dioxide (DTD)) for more than 100 cycles^[3]. The group stated that one possible cause of this remarkably high cycle life came from the decomposition of LiDFOB at the cathode. The oxidation of LiDFOB at the cathode produces LiBF₄ which is beneficial for the lithium anode^[3]. The combined oxidation and reduction of LiDFOB at the cathode and

anode respectively cause a large consumption of LiDFOB. This high consumption limits the cycle life of the cell.

One of the problems of AFLMBs is their safety. Louli et al. characterised the safety of AFLMBs with a qualitative water submersion test and a nail puncture test^[3]. The submersion test was performed by submerging the plated lithium in water. Lithium plated with the dual salt 0.6 M LiDFOB + 0.6 M LiBF₄ FEC:DEC 1:2 v/v electrolyte after 20 and 80 cycles were tested. Lithium plated with a single salt 1.2 M LiPF₆ FEC:DEC 1:2 v/v electrolyte after 20 and 80 cycles was also tested. A charged graphite anode was also tested for reference. The lithium from the dual salt at 20 cycles gassed and foamed at the surface of the water, the same result as the charged graphite anode^[3]. The lithium from the dual salt at 80 cycles produced a small flame in addition to gassing and foaming^[3]. The lithium from the single salt electrolyte produced large explosions when submerged^[3]. This indicated that the surface area of the deposited lithium may be a factor in the safety of a AFLMB. A puncture test was performed with full AFLMB cells. All cells were at top of charge after 1, 20 and 50 cycles. A cell using the previously mentioned dual salt electrolyte, a cell using a 1.73 M LiFSI (DME):1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE) electrolyte, and a cell using a 4 M LiFSI FEC:DEC electrolyte were tested. A thermocouple at the tip of the nail measured the temperature during the puncture test. The dual salt electrolyte cell exhibited temperature increase with a increased number of cycles, but never exceeded 100 °C^[3]. Both of the other cells also exhibited an increase in temperature with cycles, but after 50 cycles the chemistry of the cells caused an explosion resulting in a temperature >300 °C^[3]. This once again suggests that the safety of the battery is dependent on the morphology of deposited lithium. The increased surface area of the dendritic and mossy lithium may cause the reactions with water or air to occur faster and more violently. This shows that an improvement in the homogeneity of deposited lithium has benefits for the safety of the battery, not just cycle life.

Anode free lithium metal batteries are still quite far away from commercialization. The best performing AFLMBs the author has knowledge of currently, using all previously mentioned techniques, outperform LIBs in initial energy density, but falls behind in cycle life and safety. Louli et al. tested a cell stack using 2 M LiDFOB + 1.4 M LiBF₄ electrolyte operating at 40 °C and 1170 kPa that retained greater energy density than a lithium ion battery (NMC532 | graphite, 1.2 M LiPF₆ EC:EMC + 2% VC + 1% (DTD)) for 200 cycles^[3]. LIBs used in practical applications today have a estimated cycle life of 1000 cycles^[4]. The safety of LIBs^[26] is better than AFLMBs for all relevant points. Although AFLMBs show greater initial energy density the poor cycle life and safety concerns rule out the use of AFLMBs in practical applications.

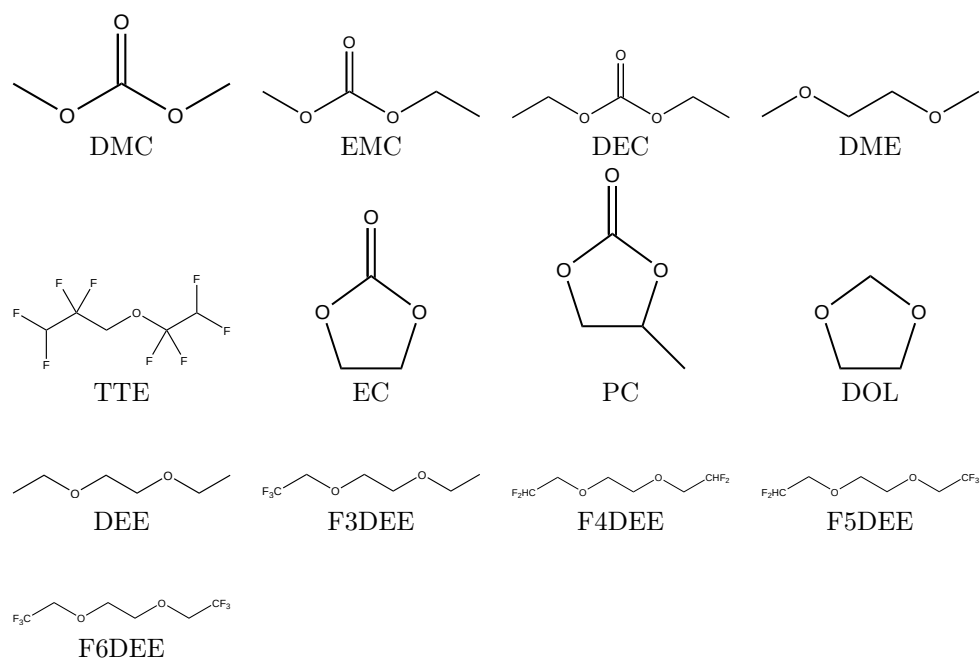


Figure 3: Chemical structure of electrolyte solvents mentioned in this thesis

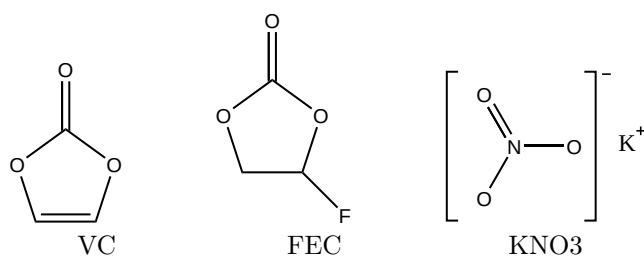


Figure 4: Chemical structure of additives mentioned in this thesis

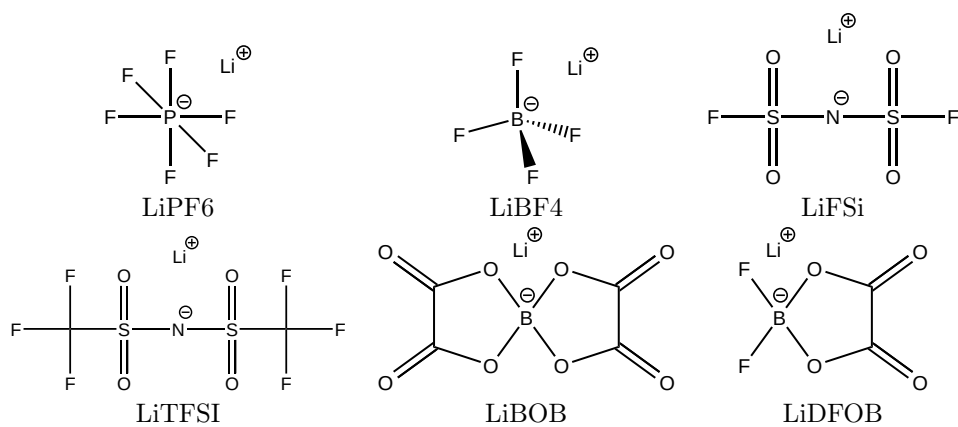


Figure 5: Chemical structure of lithium salts mentioned in this thesis

4 Conclusion

The advantages and challenges of anode free lithium ion has been discussed with a focus on electrolyte design, solid electrolyte interface and lithium morphology. The characteristics that make for a good electrolyte and why it is hard to achieve an ideal SEI has been discussed. The creation of a strong ionically conductive SEI has been identified as a necessity for favourable lithium morphology. The deposition of an ideally flat homogeneous lithium morphology has been shown to be important in the reversibility of the deposition/stripping of lithium during battery cycling.

Today's best performing electrolytes are concentrated dual salt electrolytes which separate the SEI creating salt from the conductive salt. This helps achieve a mechanically stable SEI with good ionic conductivity, while retaining the conductivity of the electrolyte. This SEI facilitates a homogeneous flat lithium deposition. This flat lithium deposition shows better reversibility and safety. The AFLMB with the performance currently outperforms a LIB in initial energy density, but falls behind in cycle life and safety.

The cycle life and safety of the battery remains too poor for any practical applications, even with the optimized electrolyte. AFLMBs show great promise with a great deal of improvement having been achieved recently. This improvement points to possible widespread adoption in the future, but more research into stabilizing the deposited lithium's morphology is needed to see this adoption.

References

- [1] M. Armand and J.-M. Tarascon. Building better batteries. *Nature*, 451(7179):652–657, February 2008. ISSN 0028-0836, 1476-4687. doi: 10.1038/451652a. URL <http://www.nature.com/articles/451652a>.
- [2] Mario Marinaro, Dominic Bresser, Engelbert Beyer, Peter Faguy, Kei Hosoi, Hong Li, Julija Sakovica, Khalil Amine, Margret Wohlfahrt-Mehrens, and Stefano Passerini. Bringing forward the development of battery cells for automotive applications: Perspective of R&D activities in China, Japan, the EU and the USA. *Journal of Power Sources*, 459:228073, May 2020. ISSN 0378-7753. doi: 10.1016/j.jpowsour.2020.228073. URL <https://www.sciencedirect.com/science/article/pii/S0378775320303761>.
- [3] A. J. Louli, A. Eldesoky, Rochelle Weber, M. Genovese, Matt Coon, Jack deGooyer, Zhe Deng, R. T. White, Jaehan Lee, Thomas Rodgers, R. Petibon, S. Hy, Shawn J. H. Cheng, and J. R. Dahn. Diagnosing and correcting anode-free cell failure via electrolyte and morphological analysis. *Nature Energy*, 5(9):693–702, September 2020. ISSN 2058-7546. doi: 10.1038/s41560-020-0668-8. URL <https://www.nature.com/articles/s41560-020-0668-8>. Number: 9 Publisher: Nature Publishing Group.
- [4] Michel Armand, Peter Axmann, Dominic Bresser, Mark Copley, Kristina Edström, Christian Ekberg, Dominique Guyomard, Bernard Lestriez, Petr Novák, Martina Petranikova, Willy Porcher, Sigita Trabesinger, Margret Wohlfahrt-Mehrens, and Heng Zhang. Lithium-ion batteries – Current state of the art and anticipated developments.

- Journal of Power Sources*, 479:228708, December 2020. ISSN 0378-7753. doi: 10.1016/j.jpowsour.2020.228708. URL <https://www.sciencedirect.com/science/article/pii/S0378775320310120>.
- [5] Christian Heubner, Sebastian Maletti, Henry Auer, Juliane Hüttel, Karsten Voigt, Oliver Lohrberg, Kristian Nikolowski, Mareike Partsch, and Alexander Michaelis. From Lithium-Metal toward Anode-Free Solid-State Batteries: Current Developments, Issues, and Challenges. *Advanced Functional Materials*, 31(51):2106608, 2021. ISSN 1616-3028. doi: 10.1002/adfm.202106608. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/adfm.202106608>. _eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/adfm.202106608>.
- [6] Zhengkun Xie, Zhijun Wu, Xiaowei An, Xiyan Yue, Jiajia Wang, Abuliti Abudula, and Guoqing Guan. Anode-free rechargeable lithium metal batteries: Progress and prospects. *Energy Storage Materials*, 32:386–401, November 2020. ISSN 2405-8297. doi: 10.1016/j.ensm.2020.07.004. URL <https://www.sciencedirect.com/science/article/pii/S2405829720302695>.
- [7] Yuan Tian, Yongling An, Chuanliang Wei, Huiyu Jiang, Shenglin Xiong, Jinkui Feng, and Yitai Qian. Recently advances and perspectives of anode-free rechargeable batteries. *Nano Energy*, 78:105344, December 2020. ISSN 2211-2855. doi: 10.1016/j.nanoen.2020.105344. URL <https://www.sciencedirect.com/science/article/pii/S2211285520309216>.
- [8] Zhiao Yu, Paul E. Rudnicki, Zewen Zhang, Zhuojun Huang, Hasan Celik, Solomon T. Oyakhire, Yuelang Chen, Xian Kong, Sang Cheol Kim, Xin Xiao, Hansen Wang, Yu Zheng, Gaurav A. Kamat, Mun Sek Kim, Stacey F. Bent, Jian Qin, Yi Cui, and Zhenan Bao. Rational solvent molecule tuning for high-performance lithium metal battery electrolytes. *Nature Energy*, 7(1):94–106, January 2022. ISSN 2058-7546. doi: 10.1038/s41560-021-00962-y. URL <https://www.nature.com/articles/s41560-021-00962-y>. Number: 1 Publisher: Nature Publishing Group.
- [9] K. Zaghbi, A. Guerfi, P. Hovington, A. Vijh, M. Trudeau, A. Mauger, J. B. Goodenough, and C. M. Julien. Review and analysis of nanostructured olivine-based lithium rechargeable batteries: Status and trends. *Journal of Power Sources*, 232:357–369, June 2013. ISSN 0378-7753. doi: 10.1016/j.jpowsour.2012.12.095. URL <https://www.sciencedirect.com/science/article/pii/S0378775312019490>.
- [10] J. Nunes-Pereira, C. M. Costa, and S. Lanceros-Méndez. Polymer composites and blends for battery separators: State of the art, challenges and future trends. *Journal of Power Sources*, 281:378–398, May 2015. ISSN 0378-7753. doi: 10.1016/j.jpowsour.2015.02.010. URL <https://www.sciencedirect.com/science/article/pii/S0378775315002335>.
- [11] Ujwal Shreenag Meda, Libin Lal, Sushantha M, and Paridhi Garg. Solid Electrolyte Interphase (SEI), a boon or a bane for lithium batteries: A review on the recent advances. *Journal of Energy Storage*, 47:103564, March 2022. ISSN 2352-152X. doi: 10.1016/j.est.2021.103564. URL <https://www.sciencedirect.com/science/article/pii/S2352152X21012433>.

- [12] Tamene Tadesse Beyene, Hailemariam Kassa Bezabh, Misganaw Adigo Weret, Teklay Mezgebe Hagos, Chen-Jui Huang, Chia-Hsin Wang, Wei-Nien Su, Hongjie Dai, and Bing-Joe Hwang. Concentrated Dual-Salt Electrolyte to Stabilize Li Metal and Increase Cycle Life of Anode Free Li-Metal Batteries. *Journal of The Electrochemical Society*, 166(8):A1501, May 2019. ISSN 1945-7111. doi: 10.1149/2.0731908jes. URL <https://iopscience.iop.org/article/10.1149/2.0731908jes/meta>. Publisher: IOP Publishing.
- [13] Ji-Guang Zhang. Anode-less. *Nature Energy*, 4(8):637–638, August 2019. ISSN 2058-7546. doi: 10.1038/s41560-019-0449-4. URL <https://www.nature.com/articles/s41560-019-0449-4>. Number: 8 Publisher: Nature Publishing Group.
- [14] Laisuo Su, Harry Charalambous, Zehao Cui, and Arumugam Manthiram. High-efficiency, anode-free lithium–metal batteries with a close-packed homogeneous lithium morphology. *Energy & Environmental Science*, 15(2):843–854, February 2022. ISSN 1754-5706. doi: 10.1039/D1EE03103A. URL <https://pubs.rsc.org/en/content/articlelanding/2022/ee/d1ee03103a>. Publisher: The Royal Society of Chemistry.
- [15] Jie Xiao, Qiuyan Li, Yujing Bi, Mei Cai, Bruce Dunn, Tobias Glossmann, Jun Liu, Tetsuya Osaka, Ryuta Sugiura, Bingbin Wu, Jihui Yang, Ji-Guang Zhang, and M. Stanley Whittingham. Understanding and applying coulombic efficiency in lithium metal batteries. *Nature Energy*, 5(8):561–568, August 2020. ISSN 2058-7546. doi: 10.1038/s41560-020-0648-z. URL <https://www.nature.com/articles/s41560-020-0648-z>. Number: 8 Publisher: Nature Publishing Group.
- [16] Zizheng Tong, Behrouz Bazri, Shu-Fen Hu, and Ru-Shi Liu. Interfacial chemistry in anode-free batteries: challenges and strategies. *Journal of Materials Chemistry A*, 9(12):7396–7406, 2021. doi: 10.1039/D1TA00419K. URL <https://pubs.rsc.org/en/content/articlelanding/2021/ta/d1ta00419k>. Publisher: Royal Society of Chemistry.
- [17] M. S. Hossain Lipu, M. A. Hannan, Aini Hussain, M. M. Hoque, Pin J. Ker, M. H. M. Saad, and Afida Ayob. A review of state of health and remaining useful life estimation methods for lithium-ion battery in electric vehicles: Challenges and recommendations. *Journal of Cleaner Production*, 205:115–133, December 2018. ISSN 0959-6526. doi: 10.1016/j.jclepro.2018.09.065. URL <https://www.sciencedirect.com/science/article/pii/S0959652618327793>.
- [18] A. J. Louli, A. Eldesoky, Rochelle Weber, M. Genovese, Matt Coon, Jack deGooyer, Zhe Deng, R. T. White, Jaehan Lee, Thomas Rodgers, R. Petibon, S. Hy, Shawn J. H. Cheng, and J. R. Dahn. Supplementary information - Diagnosing and correcting anode-free cell failure via electrolyte and morphological analysis. *Nature Energy*, 5(9):693–702, September 2020. ISSN 2058-7546. doi: 10.1038/s41560-020-0668-8. URL <https://www.nature.com/articles/s41560-020-0668-8>.
- [19] Ingeborg Treu Røe and Sondre Kvalvåg Schnell. Slow surface diffusion on Cu substrates in Li metal batteries. *Journal of Materials Chemistry A*, 9(17):11042–11048, May 2021. ISSN 2050-7496. doi: 10.1039/D1TA02300D. URL <https://pubs.rsc.org/en/content/articlelanding/2021/ta/d1ta02300d>. Publisher: The Royal Society of Chemistry.

- [20] Jie Xiao. How lithium dendrites form in liquid batteries. *Science*, 366(6464):426–427, October 2019. doi: 10.1126/science.aay8672. URL <https://www.science.org/doi/10.1126/science.aay8672>. Publisher: American Association for the Advancement of Science.
- [21] A. J. Louli, Matthew Genovese, Rochelle Weber, S. G. Hames, E. R. Logan, and J. R. Dahn. Exploring the Impact of Mechanical Pressure on the Performance of Anode-Free Lithium Metal Cells. *Journal of The Electrochemical Society*, 166(8):A1291, April 2019. ISSN 1945-7111. doi: 10.1149/2.0091908jes. URL <https://iopscience.iop.org/article/10.1149/2.0091908jes/meta>. Publisher: IOP Publishing.
- [22] Rochelle Weber, Matthew Genovese, A. J. Louli, Samuel Hames, Cameron Martin, Ian G. Hill, and J. R. Dahn. Long cycle life and dendrite-free lithium morphology in anode-free lithium pouch cells enabled by a dual-salt liquid electrolyte. *Nature Energy*, 4(8):683–689, August 2019. ISSN 2058-7546. doi: 10.1038/s41560-019-0428-9. URL <https://www.nature.com/articles/s41560-019-0428-9>. Number: 8 Publisher: Nature Publishing Group.
- [23] N.A. Sahalie, A.A. Assegie, W.-N. Su, Z.T. Wondimkun, B.A. Jote, B. Thirumalraj, C.-J. Huang, Y.-W. Yang, and B.-J. Hwang. Effect of bifunctional additive potassium nitrate on performance of anode free lithium metal battery in carbonate electrolyte. *Journal of Power Sources*, 437, 2019. ISSN 0378-7753. doi: 10.1016/j.jpowsour.2019.226912.
- [24] Jiangfeng Qian, Brian D. Adams, Jianming Zheng, Wu Xu, Wesley A. Henderson, Jun Wang, Mark E. Bowden, Suochang Xu, Jianzhi Hu, and Ji-Guang Zhang. Anode-Free Rechargeable Lithium Metal Batteries. *Advanced Functional Materials*, 26(39):7094–7102, 2016. ISSN 1616-3028. doi: 10.1002/adfm.201602353. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/adfm.201602353>. _eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/adfm.201602353>.
- [25] Sunhyung Jurng, Zachary L. Brown, Jiyeon Kim, and Brett L. Lucht. Effect of electrolyte on the nanostructure of the solid electrolyte interphase (SEI) and performance of lithium metal anodes. *Energy & Environmental Science*, 11(9):2600–2608, September 2018. ISSN 1754-5706. doi: 10.1039/C8EE00364E. URL <https://pubs.rsc.org/en/content/articlelanding/2018/ee/c8ee00364e>. Publisher: The Royal Society of Chemistry.
- [26] Shin-ichi Tobishima, Koji Takei, Yoji Sakurai, and Jun-ichi Yamaki. Lithium ion cell safety. *Journal of Power Sources*, 90(2):188–195, October 2000. ISSN 0378-7753. doi: 10.1016/S0378-7753(00)00409-2. URL <https://www.sciencedirect.com/science/article/pii/S0378775300004092>.

