19-673 Project report

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1: Field analysis study

1.1 Field of interest

The field of interest is polymer-containing anode protective layer(s) for lithium metal batteries.

Lithium metal batteries are rechargeable electrochemical energy storage devices that utilize lithium metal (usually in the form of a foil or a deposited layer) as the negative electrode, also referred to as the anode. Typically, the cathode, or the positive electrode, comprises lithium transition metal oxide particle aggregates, although other electrochemically active materials may also be used (such as sulfur, oxygen, CFx etc.). Lithium-ion batteries, on the other hand, uses as anode at least one of particles of any carbon (such as graphite, coke, hard carbons, graphene) or particles of a metal (such as silicon or tin). Lithium metal batteries possess superior specific energy (energy/weight ratio) and energy density (energy/volume ratio) as compared to lithium-ion batteries. However, they suffer from serious issues of safety and low efficiency stemming from the high reactivity of the lithium and non-uniform deposition of the lithium metal during charging.

Several different approaches have been used in the literature to attempt to solve the challenges stemming from the use of lithium metal at the anode. One strategy is to incorporate additives into the liquid electrolyte that react with the lithium metal and form a film of decomposition products in-situ at the lithium metal-electrolyte interface that prevent further reaction and stabilize the interface. Another strategy is to use a solid electrolyte facing the lithium metal and use a liquid electrolyte (called catholyte) at the cathode side; essentially, the porous polymer separator is replaced by a non-porous ceramic solid separator. Another strategy completely eliminates the liquid electrolyte at both the electrodes and is called an all-solid-state battery. Another strategy is to coat the lithium metal foil or layer with a protective layer ex-situ; this may be used in conjunction with a solid electrolyte or a conventional liquid catholyte. The processes used to dispose the protective layer on the lithium metal foil/layer ensures conformal contact between the protective layer and the lithium metal, in contrast with the strategy of using solid electrolytes, which does not have perfect conformal contact with the lithium metal. Certain inventions may utilize more than one of the strategies described above. The patents analyzed in this project relate to inventions of protective layer for lithium metal batteries, specifically polymer-containing protective layer.

1.2 Selected patents

Sl. No.	Patent No.	Title	Assignee	# of claims	Independent claims
1	US10741846B2	Negative electrode for lithium metal battery and lithium metal battery comprising the same	Samsung Electronics Co Ltd, Samsung SDI Co Ltd	22	1, 18, 22
2	US10847799B2	Negative electrode for lithium metal battery and lithium metal battery comprising the same	Samsung Electronics Co Ltd, Samsung SDI Co Ltd	17	1, 10, 17
3	US10608249B2	Conformal coating of lithium anode via vapor deposition for rechargeable lithium ion batteries	University of California, GM Global Technology Operations LLC	20	1, 10
4	US10777810B2	Lithium metal secondary battery containing a protected lithium anode	Global Graphene Group Inc	30	1
5	US10784509B2	Lithium metal secondary battery containing two anode-protecting layers	Global Graphene Group Inc	26	1
6	US10483547B2	Lithium metal battery	Samsung Electronics Co Ltd, Samsung SDI Co Ltd	23	1
7	US10573933B2	Lithium metal battery	Samsung Electronics Co Ltd	27	1, 26, 27
8	US10497927B2	Methods of applying self-forming artificial solid electrolyte interface (SEI) layer to stabilize cycle stability of electrodes in lithium batteries	GM Global Technology Operations LLC	18	1, 11, 16
9	US10347904B2	Multi-layer polymer coated Li anode for high density Li metal battery	SES Holdings Pte Ltd, General Motors Ventures LLC	20	1
10	US10770721B2	Lithium metal secondary battery containing anode-protecting polymer layer and manufacturing method	Global Graphene Group Inc	37	1

1.3 Summary of selected patents

All the chosen patents have been invented to improve the performance of a lithium metal anode (negative electrode) in a lithium-based battery, and more specifically are inventions for polymeric and polymer-ceramic composite coatings that are to be applied directly on to the lithium metal anode prior to assembly into an electrochemical cell. The exact problem that all the inventions solve is to suppress the reaction between the lithium metal and the other components inside the electrochemical cell by acting as a physical barrier to such reactions, as well as preventing the growth of dendrites during lithium deposition while charging, while allowing transport of lithium ions through the barrier. The exact advantage of each invention over the other inventions in the list summarized above depends on the specifics of that invention and is summarized below.

1. US10741846B2:
In this invention, the inventors have developed a protective layer for a lithium metal anode comprising at least one primary particle having sizes between 1 µm to 100 µm, made of organic, inorganic or a mixture of organic and inorganic compound(s), with a crosslinked material including a polymerizable oligomer interspersed between the primary particle(s). The crosslinked material including the polymerizable oligomer helps fill the pores between the primary particles, thereby preventing the percolation of the electrolyte (if a liquid electrolyte is used) or any liquid contained in the electrochemical cell on to the lithium metal surface and cause side reactions leading to the consumption of lithium metal and/or the electrolyte and/or any liquid contained in the electrochemical cell, thereby resulting in reduced cell lifetime. Some embodiments of the invention incorporate the use of polymers with very poor wettability with the electrolyte, which further suppress electrolyte and/or liquid percolation through voids. The inventors also claim that the protective layer may have improved mechanical properties due to the integration of primary particles (which may be composed of material that is brittle) into a polymeric matrix.

2. US10847799B2:
In this invention, the inventors have developed a negative electrode comprising a lithium metal electrode and a protective layer for said lithium metal electrode comprising at least one primary particle having sizes between 1 µm to 100 µm, made of organic, inorganic or a mixture of organic and inorganic compound(s). Also claimed is a method to manufacture the negative electrode, and an invention for a lithium metal battery incorporating the negative electrode. Unlike the previous invention, the primary particle(s) are not interspersed with a polymeric material. The negative electrode, when included with a liquid electrolyte, may have enhanced ionic conductivity due to the availability of ion conducting paths around the primary particles. The inventors claim that this invention may enable the manufacture of lithium metal batteries with stable charge-discharge cycle characteristics.

3. US10608249B2:
In this invention, the inventors have developed a negative electrode comprising a lithium metal electrode and a protective layer for said lithium metal electrode, as well as a method to manufacture the negative electrode that involves using a vapor deposition process to deposit two precursors

onto the exposed surface of the lithium metal electrode. The two precursors react to form a surface coating comprising inorganic and organic particles. The first precursor includes an organic mercapto-containing silane, and the second precursor includes an inorganic silane. The use of such a vapor deposition process is expected to improve the ease of deposition of the protective layer for large-scale manufacture, as well as offer precise control over the size and distribution of the inorganic particles.

4. US10777810B2:
In this invention, the inventors have developed a lithium secondary (i.e., rechargeable) battery including a negative electrode (i.e., anode) comprising lithium metal or lithium alloy active material, a first protective layer comprising a lithium ion conducting material with specified range of thicknesses and specified range of lithium-ion conductivities, and a second protective layer comprising an elastomer with specified range of thicknesses, specified range of fully recoverable tensile elastic strain and specified range of lithium-ion conductivities. The material for the first layer (disposed between the lithium metal surface and the second layer) may be a lithium-containing ceramic, a lithium salt, lithium-ion conducting polymer or a solid-state electrolyte. The usage of just 2 layers as opposed to three or more layers (claimed in previous inventions) is advantageous due to the reduced complexity and lower cost. The inventors claim that certain other previous inventions use materials or processes to deposit the films that are expensive and laborious, unlike their invention.

Previous inventions that utilize a solid electrolyte suffer from low lithium-ion conductivity as well as poor contact with the lithium metal, which reduces the effectiveness of the electrolyte and hinders the battery from functioning effectively, especially at low temperatures. Though the use of liquid electrolytes is desirous due to better contact and higher conductivity, the reactivity of liquid electrolytes with the lithium metal resulting in the depletion of both is undesirable. The use of the patented two-film deposition process is claimed to reduce the side reactions that would otherwise occur between the liquid electrolyte and the lithium metal, as well as provide a surface with enhanced contact with the solid electrolyte, if a solid electrolyte were to be used in the electrochemical cell.

5. US10784509B2:
In this invention, the inventors have developed a lithium secondary (i.e., rechargeable) battery including a negative electrode (i.e., anode) comprising lithium metal or lithium alloy active material, a first protective layer comprising a lithium ion conducting material with specified range of thicknesses and minimum specific surface area of 50 m^2/g, and a second protective layer comprising an elastomer with specified range of thicknesses, specified range of fully recoverable tensile elastic strain and specified range of lithium-ion conductivities. The material for the first layer (disposed between the lithium metal surface and the second layer) comprises an electron-conducting material selected from graphene sheets, carbon nanotubes, carbon nanofibers, carbon or graphite fibers, expanded graphite flakes, metal nanowires and conductive polymer fibers.

This invention is very similar to the previous invention, and even has the same inventors and assignee. However, this invention differs from the previous invention with respect to the choice of material for the first layer that is deposited to be in contact with the lithium metal layer. The previous invention utilizes a first layer comprising a lithium-based compound which need not be electron-conducting, whereas this invention utilizes an electron-conducting material for the first layer, including carbon-based materials.

6. US10483547B2:

In this invention, the inventors have developed a lithium metal battery utilizing a liquid electrolyte and a lithium metal anode. The lithium metal anode includes a lithium-containing active material and a protective coating (on the lithium-containing active material) comprising a polymer and at least one selected from a metal salt including a group 1 and group 2 element and a nitrogen-containing additive, wherein the non-polymeric second component of the protective layer is insoluble in the liquid electrolyte.

Previous inventions proposed the use of cesium salt(s) as additives to the liquid electrolyte to suppress dendritic deposition of lithium, or the use of a polymer electrolyte as a lithium metal protective layer. The inventors claim that the use of cesium salt as an additive is impractical due to its insolubility in the liquid electrolyte as well as participating in the electrochemical reaction at the cathode, thereby deteriorating cell performance. They also claim that the use of polymer electrolytes as protective coatings may increase the interfacial resistance between the lithium metal and the polymer electrolyte coating. The inventors claim that their invention solves both of these problems based on their extensive research.

7. US10573933B2:

In this invention, the inventors have developed a lithium metal battery utilizing a liquid electrolyte and a lithium metal anode covered with an amorphous protective layer comprising a polymer selected from at least one of poly(vinyl alcohol) and a poly(vinyl alcohol) blend. The inventors claim that the use of a polar polymer suppresses reaction with the non-polar electrolyte more effectively, as well as stabilizing the lithium metal-liquid electrolyte interface by ensuring uniform current and ion distribution on the lithium metal surface, thereby suppressing dendritic deposition of lithium. The inventors also claim that unlike coating materials in similar art, the invented coating material possesses excellent chemical resistance to typical liquid electrolytes, as well as achieving more effective suppression of short-circuits inside the cell caused due to cracks in the protective layer. Additionally, the inventors claim that the protective layer they invented binds more strongly with the lithium metal and is hence more resistant to peeling away from the lithium metal, as well as possessing superior mechanical properties such as elongation and tensile modulus.

8. US10497927B2:

This patent covers an invention for a method of making an anode via the application of a fluoropolymer to the surface of any one of lithium metal, silicon metal or silicon-containing alloys through a deposition process. The fluoropolymer reacts with the lithium to form a polymer matrix composite composed of particles of lithium fluoride embedded in a polymer matrix. The patent also covers an invention for electrochemical cells that incorporate said anode. The key advantage of this process is that the composite structure of the protective layer is formed in-situ via a single-step deposition process, as opposed to other processes which may require multiple steps and are hence likely to be more laborious and expensive.

9. US10347904B2:
This patent covers an invention for a multi-layer protective polymer coating on the exposed surface of a lithium metal containing anode. The multi-layer coating includes an outer polymeric crosslinked gel layer that includes a first polymer, a soft segment polymer and an electrolyte, and an inner polymeric layer (disposed between the outer polymeric crosslinked gel layer and the lithium metal surface) comprising a second polymer. The inner polymer layer is claimed to provide mechanical strength to the coating and may protect the lithium metal layer by functioning as a barrier. The inventors claim that the use of multiple layers of a certain specific thickness offers better protection to the lithium metal anode as compared to the use of a single layer coating of the same specific thickness. Furthermore, the inventors claim that the manufacturing process may use dip coating, which is a low-cost and scalable coating process when compared to vapor deposition processes used by other inventions.

10. US10770721B2:
This patent covers an invention for a rechargeable lithium battery wherein the anode comprises a lithium-containing active material coated with a thin layer of a polymer of a certain specified range of thicknesses, a certain specified range of lithium-ion conductivities at room temperature and certain specified range of recoverable tensile strains, wherein the polymer layer comprises an ultrahigh molecular weight polymer having a molecular weight within a certain specified range of molecular weights. The inventors claim that anode protective layers in previous inventions may utilize expensive materials, difficult processes or complex anode structures and yet failed to yield a lithium metal anode with satisfactory performance, a problem their invention is claimed to solve. Moreover, the inventors claim that the elastic properties of the polymer film in their invention are designed so as to prevent loss of contact between the polymer film and the lithium metal, thereby ensuring successful re-deposition of lithium on to the lithium metal.

1.4 Summary of patent themes

1.3.1 Enabling lithium metal anode via protective coating in rechargeable lithium batteries

Current rechargeable lithium batteries use anodes comprising at least one of graphite or silicon particles. Substituting these particles with lithium metal, typically in the form of a foil, helps reduce the overall weight of the cell, thereby improving the specific energy (defined as the cell energy to cell weight ratio) and energy density (defined as the cell energy to cell volume ratio) of the cell. However, the high reactivity of the lithium metal towards the electrolyte results in the loss of lithium inventory at the anode as well as electrolyte degradation. As a result, a non-trivial fraction of the lithium deposited at the anode during charging gets lost to these side reactions, thereby resulting in capacity loss and premature death of the cell. Moreover, the heterogeneity in the thickness and composition of the decomposition layer at the lithium metal-electrolyte interface causes lithium to deposit selectively at certain locations during charging, which subsequently grow with each charge cycle into needle-like structures, called dendrites, that eventually reach the cathode, thereby causing an internal short circuit. Therefore, suppressing the reaction between the electrolyte and the lithium metal may yield a lithium rechargeable battery with superior performance. All the patents discussed above cover inventions designed to suppress reaction between the electrolyte and the lithium metal via the application of a protective coating on the lithium metal surface which acts as a barrier to such reactions.

1.3.2 Inventions claiming lithium metal battery

US Patents US10741846B2, US10847799B2, US10777810B2, US10784509B2, US10483547B2, US10573933B2, US10497927B2, US10347904B2 and US10770721B2 claim invention of a lithium metal battery.

1.3.3 polymer matrix composite coatings

Polymer matrix composite coatings consist of primary particles of organic or inorganic particles dispersed in a polymer matrix, which together constitute the polymer matrix composite coating. US10741846B2, US10608249B2, US10483547B2 and US10497927B2 each describe the resultant coating to consist of primary particles dispersed in a polymer matrix. Among these, US10608249B2 and US10497927B2 cover inventions where the composite coatings form in-situ via reaction between the deposited film and lithium, or via reaction between the components of the deposited film.

1.3.4 Inventions for lithium metal batteries with a liquid electrolyte

The following inventions have claims for a lithium battery that utilize a liquid electrolyte (mentioned explicitly): US10741846B2, US10847799B2, US10483547B2, US10573933B2. Certain inventions not in the list in this paragraph comprise claims for lithium metal batteries using an electrolyte, without specific mention to the nature of the electrolyte (i.e., solid, liquid or gel electrolyte).

1.3.5 All patents have at least one inventor of Asian origin

All patents have at least one inventor of Asian origin.

1.5 Patents claims analysis

1. US10741846B2:

The simplest design around for claim 1 of this patent is to swap the chemical identities of the first particle(s) and the crosslinked material interspersed between the first particle(s) i.e., the first particle of the plurality of first particles comprises an acrylate group, and the polymerizable oligomer interspersed between the primary particles comprises a polymer comprising a styrene unit. This does not significantly alter the makeup of the protective coating and is therefore likely to have the same performance benefits of the patented invention. Additionally, the manufacturing steps require only slight modification (swapping the precursors in the steps that introduce the first particles and the crosslinked polymer) and is therefore highly likely to work.

Yes, implementing the invention in claim 1 of this patent would infringe claim 1 of US10847799B2 (the second patent). Claim 1 of the second patent is an invention for a negative electrode comprising a lithium metal electrode and a protective layer on the lithium metal electrode comprising a mixture of a lithium salt and particles of polystyrene. Claim 1 of this infringing patent is an invention for a negative electrode comprising a lithium metal electrode and a protective layer on the lithium metal electrode comprising a mixture of a lithium salt and particles of polystyrene of the same size as the second patent, and a crosslinked polymer dispersed between the particles. Thus, claim 1 of this patent is narrower than claim 1 of the second patent.

2. US10847799B2:

The simplest design around for claim 1 of this patent is to substitute the chemical identity of the organic particles. One possible (non-limiting) example would be to use particles comprising an acrylate group instead of using particles comprising styrene group. In the detailed description of this patent, it was claimed by the inventors that when the claimed invention is used with a liquid electrolyte, the liquid electrolyte may form ion conducting paths around the particles that constitute the protective layer and therefore changing the chemical identity of the particles from styrene units to acrylate units is unlikely to significantly affect the working of the invention. Designing around claim 1 of this patent by using particles larger than the specified 100 µm could also be used, though using particles that are significantly larger than in the claimed invention may interfere with the working principle, leading to an invention that works less effectively than the claimed invention.

Though claim 1 of this patent does not infringe claim 1 of other patents, it is very similar to claim 1 of the first patent (US10741846B2). Claim 1 of both patents claim an invention for a negative electrode for a lithium metal battery, comprising a lithium metal electrode and a protective layer comprising a mixture of a lithium salt and organic particles of polystyrene having same or similar mechanical properties and particle size specifications. Claim 1 of the first patent (US10741846B2) incorporates a polymer material interspersed in between the particles, which claim 1 of the this (second) patent does not.

3. US10608249B2:

Claim 1 of this patent can be designed around by substituting the first precursor comprising a mercapto-containing silane with a first precursor comprising a non-mercapto-containing silane. Alternatively, we may use a small quantity of an additional third precursor comprising a non-mercapto-containing silane in addition to the two precursors of claim 1 such that the effect of the third precursor on the coating and the cell performance is negligible. This ensures that not all of the steps of this method patent are followed exactly, thereby designing around this patent effectively.

Though claim 1 of this patent does not infringe claim 1 of other patents, it is very similar to claim 1 of the eighth patent (US10497927B2). Both patents claim an invention for a negative lithium-containing electrode comprising a lithium metal electrode with an inorganic-organic composite surface coating enabled via deposition of one or more precursors on to the lithium metal surface. This patent uses two precursors that react to form the composite surface coating, whereas claim 1 of the eighth patent uses a single precursor that reacts with the lithium to form the composite surface coating.

4. US10777810B2:

Claim 1 of this patent could be designed around by depositing as the second anode-protecting layer an inorganic-organic composite surface coating instead of the elastomer claimed by claim 1 of this patent. Other inventions in the set of patents have shown in detail the methods to deposit such a coating; the proposed design-around is thus deemed to be feasible. It must be noted that not all methods to deposit the inorganic-organic composite may work; for example, the part of the method in patent 8 (US10497927B2) relies upon the reaction between the fluorine in the deposited polymer and the lithium metal to form lithium fluoride particles that constitute the inorganic component of the composite; therefore, this process is unlikely to work when deposited on top of the first anode-protecting layer as the first anode-protecting layer would hinder or even entirely suppress the reaction with lithium that is needed to form lithium fluoride.

Claim 1 of this patent has a significant overlap with claim 1 of the fifth patent (US10784509B2). Claim 1 of both patents use the same architecture of having two anode-protecting layers applied on top of the lithium metal layer; they differ in the aspect of the material that constitutes the first anode-protecting layer. This patent does not explicitly specify the materials to be used for the first layer and only specifies the range of lithium-ion conductivities of the material to be used, while the fifth patent specifies, in a manner that may be interpreted as limiting, a list of materials that may be used for the first layer. Note that both this and the fifth patent have the same inventors and assignee and were filed just two days apart.

Claim 1 of this patent has a significant overlap with claim 1 of the ninth patent (US10347904B2). Claim 1 of both patents use the same architecture of having two anode-protecting layers applied on top of the lithium metal layer; they differ in the aspect of the material that constitutes the second outer anode-protecting layer. This patent does not explicitly specify the materials to be used for the first layer and only specifies the range of lithium-ion conductivities of the material to be used as well as the range of fully recoverable tensile elastic strain, while the ninth patent specifies the second outer layer to comprise a first polymer, a soft segment polymer and an electrolyte within a crosslinked matrix.

5. US10784509B2:
The claimed invention is a lithium metal rechargeable battery comprising an anode comprising a lithium metal/lithium alloy layer, a first anode protecting layer comprising electron-conducting material selected from a specified list of electron-conducting materials, and a second anode protecting layer comprising an elastomer of specified range of thicknesses, lithium-ion conductivities and fully recoverable tensile elastic strain. That the first layer comprise electron-conducting material is claimed by the inventors to be crucial to the working of the invention; yet the list of electron-conducting materials specified in claim 1 is non-exhaustive. Thus, we could design around claim 1 of this patent by choosing the electron-conducting material to be metal nanosheets or metal nanoparticles (or both) and retaining all other aspects of the invention.

Claim 1 of this patent has a significant overlap with claim 1 of the fourth patent (US10777810B2). Claim 1 of both patents use the same architecture of having two anode-protecting layers applied on top of the lithium metal layer; they differ in the aspect of the material that constitutes the first anode-protecting layer. This patent specifies, in a manner that may be interpreted as limiting, a list of materials that may be used for the first layer, whereas the fourth patent does not explicitly specify the materials to be used for the first layer and only specifies the range of lithium-ion conductivities and thicknesses of the material to be used. Note that both this and the fifth patent have the same inventors and assignee and were filed just two days apart.

Claim 1 of this patent has a significant overlap with claim 1 of the ninth patent (US10347904B2). Claim 1 of both patents use the same architecture of having two anode-protecting layers applied on top of the lithium metal layer; they differ in the aspect of the materials used for both the protecting layers. The first layer (in contact with the lithium metal layer) of claim 1 of this patent comprises an electron-conducting material and specifies a list of those materials, whereas the first layer of claim 1 of the ninth patent comprises a polymer. The second layer deposited over the first layer in claim 1 of this patent comprises an elastomer with specified range of fully recoverable tensile elastic strains and lithium-ion conductivities, whereas the second layer in claim 1 of the ninth patent comprises a polymeric crosslinked gel layer comprising a polymer, a soft segment polymer and an electrolyte within a crosslinked matrix.

6. US10483547B2:
Claim 1 of this patent is for a lithium metal battery. The critical bottleneck in the success of such a battery is the anode and not the cathode or the electrolyte. Claim 1 of this patent has an explicit, and in a manner that may be interpreted as limiting, requirement for the use of a liquid electrolyte. We could thus design around this claim by using a solid electrolyte instead of a liquid electrolyte. This ensures that the anode, including the protecting layer, works as intended. The use of a solid electrolyte is not a limiting factor to the proper functioning of the cell as cells that use a solid

electrolyte (referred to as an all-solid-state battery) have been made and successfully demonstrated to work by those skilled in the art.

Claim 1 of this patent has a significant overlap with claim 1 of the seventh patent (US10573933B2). Claim 1 of both inventions are for a lithium metal battery comprising a cathode, a lithium-containing anode, a liquid electrolyte disposed between the anode and the cathode, and a protective layer that includes a polymer. Claim 1 of this patent, unlike the seventh patent, claims the use of one or more cathode materials selected from a provided list of cathode materials. Claim 1 of both patents also differ with respect to the make-up of the protective layer.

Claim 1 of this patent also has a significant overlap with claim 1 of the tenth patent (US10770721B2). Claim 1 of both inventions are for a lithium metal battery comprising a cathode, a lithium-containing anode, a liquid electrolyte disposed between the anode and the cathode, and a protective layer that includes a polymer. Claim 1 of both patents differ only with respect to the make-up of the protective layer.

7. US10573933B2:
Claim 1 of this patent is an invention for a lithium metal battery with an anode comprising a protective layer comprising an amorphous polymer, wherein the mixed weight ratio of the polymer to the lithium salt is in a range of 3:1 to 3:8. This patent could be designed around by changing the mixed weight ratio of the polymer to the lithium salt to 4:1, which falls outside the range claimed by claim 1 of this patent and would therefore not infringe claim 1. Considering how there exist other patents in this list which use a coating that consists only of polymers, this design-around is likely to work, and the method of manufacture could be adopted from this patent itself.

Claim 1 of this patent has a significant overlap with claim 1 of the sixth patent (US10483547B2). Claim 1 of both inventions are for a lithium metal battery comprising a cathode, a lithium-containing anode, a liquid electrolyte disposed between the anode and the cathode, and a protective layer that includes a polymer. Claim 1 of the sixth patent, unlike this patent, claims the use of one or more cathode materials selected from a provided list of cathode materials. Claim 1 of both patents also differ with respect to the make-up of the protective layer.

Claim 1 of this patent also has a significant overlap with claim 1 of the tenth patent (US10770721B2). Claim 1 of both inventions are for a lithium metal battery comprising a cathode, a lithium-containing anode, a liquid electrolyte disposed between the anode and the cathode, and a protective layer that includes a polymer. Claim 1 of both patents differ only with respect to the make-up of the protective layer.

8. US10497927B2:
Claim 1 of this patent is a method of making the anode in which a fluoropolymer is applied via a deposition process to the active material contained in a prefabricated electrode layer, and the fluoropolymer reacts with the lithium to form the composite protective layer which includes lithium fluoride (formed via the reaction) embedded in a matrix of the polymer, and the thickness

of the deposited layer is 5-20 nm. We can design around this claim by depositing the same fluoropolymer to a thickness of 30 nm.

Claim 1 of this patent has a significant overlap with claim 1 of the third patent (US10608249B2). Both claims are for a method of making a lithium-containing anode in which precursor(s) are deposited through a deposition process and react to form an inorganic-organic composite surface coating. Claim 1 of this patent uses only 1 precursor that reacts with lithium to form the composite coating, whereas claim 1 of the third patent uses 2 precursors that react with each other to form the composite coating. Claim 1 of the third patent further specifies, in a manner that may be interpreted to be limiting, that the deposition process is a vapor deposition process.

Claim 1 of all the other patents in this set are not method claims (most other patents do have claims for a method to make the negative electrode, just that they are not claim 1; the question explicitly asks for a comparison of claim 1) and hence the analysis of overlap is made for patents in which claim 1 is a claim for a negative electrode. The overlap is determined based on the similarity of the end product (i.e., the negative electrode with a protective coating).

Claim 1 of this patent has significant overlap with claim 1 of the second patent (US10847799B2). Claim 1 of the second patent is for an anode for a lithium metal battery with a protective coating comprising a mixture of a polymer and a lithium salt. The product formed with the method of this (i.e., eighth) patent is an anode for a lithium metal battery with a protective coating comprising a mixture of a polymer and lithium fluoride, which is a lithium salt.

9. US10347904B2:
Claim 1 of this patent is an invention for a lithium metal anode with 2 protective layers; the inner protective layer (that is in contact with the lithium metal) comprising a polymer, and the outer protective layer (in contact with the inner protective layer and the electrolyte at the opposing surfaces) comprising a polymer, a soft segment polymer and an electrolyte within a crosslinked matrix. This can be designed around by using as the first layer an inorganic material. There exist other patents (for e.g., US10797353B2) which provide methods for making such a coating of an inorganic material; the existence of such patents also makes it likely that such a coating method would work (and yield a lithium metal battery with satisfactory performance). Inorganic materials (especially lithium-based inorganic materials) are chemically very stable and hence would not adversely react with the outer polymeric gel coating that may be applied over the inner inorganic coating.

Claim 1 of this patent has a significant overlap with claim 1 of the fourth patent (US10777810B2). Both patents claim an invention for an anode with two protecting layers of which at least one layer is a polymeric material. While this patent uses an inner polymeric layer and an outer polymeric gel layer, the fourth patent uses a lithium-ion conducting layer (that may be polymeric, though not necessarily so) as the inner layer and an elastomer as the outer layer.

Claim 1 of this patent has a significant overlap with claim 1 of the tenth patent (US10770721B2). This patent uses an inner anode-protective layer comprising a polymer; claim 1 of the tenth patent also uses an anode-protective layer comprising a polymer. Claim 1 of the tenth patent does not use a second protective layer, unlike this patent.

10. US10770721B2:
Claim 1 of this patent is for a lithium secondary battery including a protective layer for the anode comprising a polymer of specified minimum recoverable tensile strain, lithium-ion conductivity, range of thicknesses, range of molecular weights and the chemical composition of the polymer. This patent can be designed around by using a polymer having a molecular weight less than 0.5×10^6, which falls outside the range specified in claim 1.

Claim 1 of this patent has a significant overlap with claim 1 of the sixth patent (US10483547B2). Claim 1 of both inventions are for a lithium metal battery comprising a cathode, a lithium-containing anode, a liquid electrolyte disposed between the anode and the cathode, and a protective layer that includes a polymer. Claim 1 of the sixth patent, unlike this patent, claims the use of one or more cathode materials selected from a provided list of cathode materials. Claim 1 of both patents also differ with respect to the make-up of the protective layer.

Claim 1 of this patent also has a significant overlap with claim 1 of the seventh patent (US10573933B2). Claim 1 of both inventions are for a lithium metal battery comprising a cathode, a lithium-containing anode, a liquid electrolyte disposed between the anode and the cathode, and a protective layer that includes a polymer. Claim 1 of both patents differ only with respect to the make-up of the protective layer.

2: Portions of a draft patent application

2.1 New invention

The proposed invention is an anode for a lithium metal battery, the lithium-containing anode comprising 2 protective layers. The first layer (that is in direct contact with the surface of the lithium metal or lithium-containing alloy) comprises a polymer matrix comprising lithium fluoride particles. One way of forming such a layer is by depositing a fluoropolymer on to the surface of the lithium-containing active material. The fluorine in the fluoropolymer reacts chemically with the lithium to form the lithium fluoride particles. The second layer is deposited on top of and in physical contact with the first layer and comprises a polymer having thickness greater than 101 µm.

2.2 Draft claim 1

What is claimed is:

1. A lithium-containing anode for an electrochemical cell, the said anode comprising:

   a lithium metal electrode comprising lithium metal or a lithium alloy or both, and

   a protective layer disposed on at least a portion of the lithium metal electrode, the protective layer comprising:

   a first layer disposed on and in physical contact with the anode active material, the first layer comprising a plurality of first particles, wherein the plurality of first particles comprises lithium fluoride, and a polymer disposed between the plurality of first particles; and

   a second layer in physical contact with said first layer having a thickness greater than 101 µm, comprising a polymer, a polymer matrix, an organic particle, a plurality of organic particles, an inorganic particle, a plurality of inorganic particles, a metal particle, a plurality of metal particles, metal nanosheet, a plurality of a metal nanosheets, a metal nanowire, a plurality of metal nanowires, graphene sheets, carbon nanotubes, conductive polymer fibers, expanded graphite flakes, carbon fibers, graphite fibers, conductive polymer fibers or a combination thereof.

The draft claim is broad as it places no restrictions on the physical, chemical or mechanical properties of the layer such as the lithium-ion conductivity, chemical composition, recoverable tensile elastic strain or morphology of the layers, with the exception of thickness of the second layer and the constitution of the first layer. Even then, the claim does not restrict the type of polymer that constitutes the first layer, making it difficult to design-around.

The above draft claim is absolutely new in light of the previous patents identified. The first, second, third, sixth, seventh, eighth and tenth patents in the list in section 1.2 of this document include inventions for a lithium metal anode with only a single protective layer, whereas this invention incorporates two protective layers. The fourth, fifth and ninth patents include inventions for a lithium metal anode with two protective layers; however, the choice of material in each of those patents differs from the choice of material in the above draft claim. The thickness of the second layer in the above draft claim also falls outside the range of thicknesses claimed by those patents.

2.3 Draft description

FIELD OF THE INVENTION

The present disclosure relates to a lithium metal battery including an anode which includes lithium.

BACKGROUND OF THE INVENTION

Lithium-based batteries are batteries used in many applications, including consumer electronic goods such as smartphones and laptops, electric and hybrid vehicles, satellites etc. to store and release electrical energy. Current lithium-ion batteries use an anode comprising graphite particles deposited on to a current collector. During charging, lithium ions travel through the electrolyte from the cathode and get incorporated into the atomic structure of graphite particles through a process referred to as intercalation. However, the use of graphite particles increases the mass and volume of the cell without contributing to the cell capacity. Replacing the graphite particles with a lithium metal layer, typically in the form of a lithium metal foil applied over the current collector, to give a lithium metal battery would therefore increase the specific energy (energy/weight ratio of the cell) and energy density (energy/volume ratio) of lithium batteries, which is advantageous for the devices that use a lithium battery. However, upon cycling, the lithium metal deposited non-uniformly at the anode during charging in the form of needle-like structures, called dendrites, which eventually cause an internal short-circuit, resulting in battery fires. Additionally, the deposited lithium metal reacts with the electrolyte, usually a liquid electrolyte, resulting in electrolyte degradation as well as consumption of lithium metal resulting in reduced cell capacity during cycling.

Many previous attempts have been made to deposit a protective coating layer on the lithium metal anode to prevent these issues (see D. Fauteux, et al., “Secondary Electrolytic Cell and Electrolytic Process,” U.S. Pat. No. 5,434,021, Jul. 18, 1995; T. A. Skotheim, “Stabilized Anode for Lithium-Polymer Battery,” U.S. Pat. No. 5,648,187, Jul. 15, 1997; U.S. Pat. No. 5,961,672 Oct. 5, 1999). Despite these efforts, no lithium metal battery has successfully moved from lab to product available in the market. A major issue with many of these approaches is the use of a single layer protective coating. The protective coating must interface with on one side a highly reactive lithium metal anode that undergoes severe (>100%) volume expansion and contraction during charging and discharging, and interface with an electrolyte on the other side. The properties of the layer need to be optimized to ensure good contact with the lithium metal anode, good contact with the electrolyte as well as good mechanical strength to withstand the volume changes and resist dendrite penetration. It is very difficult to optimize the constitution of the layer to accomplish all three tasks effectively. An effective design of a protective layer for a lithium metal anode is needed.

SUMMARY

This section provides a general summary of the disclosure and is not a comprehensive disclosure of its full scope or all of its features.

Provided is an anode for a lithium metal battery, the anode including a two-layer coating.

According to an aspect of an exemplary embodiment, a lithium-containing anode for an electrochemical cell includes: a lithium metal electrode comprising lithium metal or a lithium alloy or both; a protective layer disposed on at least a portion of the lithium metal electrode, the protective layer comprising: a first layer disposed on and in physical contact with the anode active material, the first layer comprising a plurality of first particles, wherein the plurality of first particles comprises lithium fluoride, and a polymer disposed between the plurality of first particles; and a second layer in physical contact with said first layer having a thickness greater than 101 µm, comprising a polymer, a polymer matrix, an organic particle, a plurality of organic particles, an inorganic particle, a plurality of inorganic particles, a metal particle, a plurality of metal particles, metal nanosheet, a plurality of a metal nanosheets, a metal nanowire, a plurality of metal nanowires, graphene sheets, carbon nanotubes, conductive polymer fibers, expanded graphite flakes, carbon fibers, graphite fibers, conductive polymer fibers or a combination thereof.

Also disclosed is one method of manufacturing a lithium-containing anode for a lithium metal battery, the method including: providing a lithium-containing electrode comprising lithium metal or a lithium alloy or both; disposing a protective layer on at least a portion, preferably over the entire exposed surface, of the lithium-containing electrode, wherein the disposed protective layer is a fluoropolymer; and disposing a protective layer on at least a portion of the first layer, preferably over the entire exposed surface of the lithium-containing electrode, wherein the protective layer comprises a polymer, a polymer matrix, an organic particle, a plurality of organic particles, an inorganic particle, a plurality of inorganic particles, a metal particle, a plurality of metal particles, metal nanosheet, a plurality of a metal nanosheets, a metal nanowire, a plurality of metal nanowires, graphene sheets, carbon nanotubes, conductive polymer fibers, expanded graphite flakes, carbon fibers, graphite fibers, conductive polymer fibers or a combination thereof, wherein the thickness of the second protective layer exceeds 101 µm.

BRIEF DESCRIPTION OF THE DRAWINGS

The drawing described herein is for illustrative purposes only of an exemplary embodiment and not all possible implementations and is not intended to limit the scope of the present disclosure.

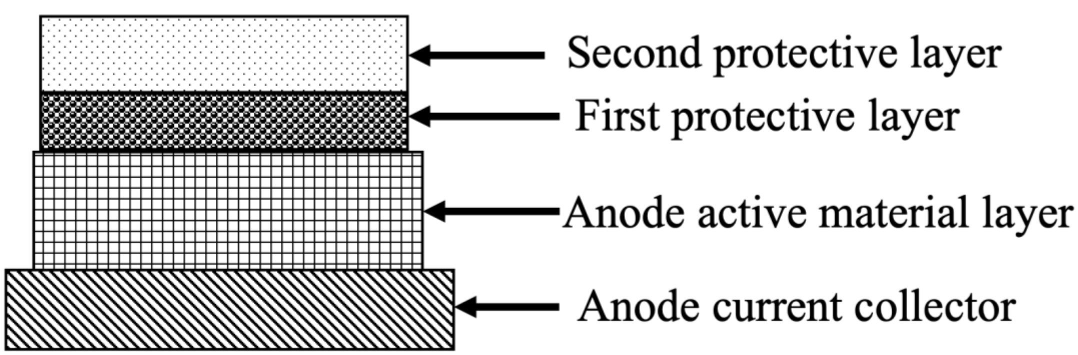

FIG. 1

FIG. 1 is a schematic cross-sectional view illustrating a structure of an exemplary embodiment of a lithium-containing anode.

DETAILED DESCRIPTION

Exemplary embodiments are described herein with reference to the cross-section illustration in figure 1 that is a schematic illustration of an idealized embodiment. As such, deviations in the shapes of the illustration resulting from, for example, manufacturing method(s) and/or tolerances, are to be expected. Thus, embodiments described herein should not be construed as limited to the particular shapes of regions as illustrated herein but are to include deviations in shapes. For example, a region illustrated or described as flat may have a rough surface and/or nonlinear features. Moreover, rounded edges are illustrated with sharp angles. The sizes and relative proportions of the regions illustrated in figure 1 are arbitrarily illustrated for better clarity in understanding. Thus, the regions illustrated in figure 1 are schematic in nature and their shapes and sizes are not intended to illustrate the precise shape and/or size of a region and are not intended to limit the scope of the present claims. All terms used herein have the same meaning as commonly understood by a person having ordinary skill in the art to which this invention belongs to.

According to an exemplary embodiment, the lithium-containing anode comprises: a current collector comprising a metal foil or a metal alloy; a lithium metal foil positioned on and in physical contact with the current collector, wherein the thickness of the lithium metal foil in the range of 10 µm to 50 µm; a first protective coating applied on at least a portion of the exposed surface of the lithium metal foil and in physical contact with the exposed surface of the lithium metal foil, wherein the average thickness of the first protective coating is 10 nm, wherein the first protective coating comprises particles of lithium fluoride embedded in a polymer matrix; and a second protective coating applied on the exposed surface of and in physical contact with the first protective coating, wherein the second protective coating comprises a polymer, wherein the average thickness of the second protective coating is 150 µm. In certain variations of said exemplary embodiment, the active material of the anode may comprise aggregates of particles of lithium metal, or particles of lithium-containing alloy, or a mixture of particles of lithium metal and lithium-containing alloys. In certain other variations of said exemplary embodiment, the thickness of the second protective coating is 200 µm.

According to another exemplary embodiment, the lithium-containing anode comprises: a current collector comprising copper foil; a lithium metal foil positioned on and in physical contact with the current collector, wherein the thickness of the lithium metal foil in the range of 20 µm to 30 µm; a first protective coating applied on at least a portion of the exposed surface of the lithium metal foil and in physical contact with the exposed surface of the lithium metal foil, wherein the average thickness of the first protective coating is 20 nm, wherein the first protective coating comprises particles of lithium fluoride embedded in a polymer matrix, wherein the polymer comprises poly(tetrafluoroethylene); and a second protective coating applied on the exposed surface of and in physical contact with the first protective coating, wherein the second protective coating comprises poly(ethylene oxide), wherein the average thickness of the second protective coating is 150 µm. In certain other variations of said exemplary embodiment, the thickness of the second protective coating is 250 µm.

Provided herein is an exemplary method of making a lithium-containing anode. The method may include positioning a lithium metal foil on the surface of and in physical contact with a current collector comprising copper foil; applying a fluoropolymer via a deposition process on one or more exposed surface of said lithium metal foil; and applying a polymer layer on one or more exposed surface of coated lithium metal foil. The applied fluoropolymer reacts chemically with the lithium-containing electrochemically active material to form an inorganic-organic composite comprising particles of lithium fluoride embedded in a polymer matrix. The manufacture of lithium metal foil and copper foil are known to those skilled in the art. Methods to apply a fluoropolymer layer on one or more exposed surface of lithium metal may be found elsewhere (X. Xiao, "Methods of applying self-forming artificial solid electrolyte interface (SEI) layer to stabilize cycle stability of electrodes in lithium batteries", U.S. Pat. No. 10,497,927, Dec. 3, 2019) and is known to those skilled in the art. Methods to apply a polymer layer or a polymer-containing composite layer on coated lithium metal may be found elsewhere (H. He et al., "Lithium metal secondary battery containing a protected lithium anode", U.S. Pat. No. 10,777,810, Sep. 15, 2020; H. He et al., "Lithium metal secondary battery containing two anode-protecting layers", U.S. Pat. No. 10,784,509, Sep. 22, 2020; M. Cho & Q. Hu, "Multi-layer polymer coated Li anode for high density Li metal battery", U.S. Pat. No. 10,347,904, Jul. 9, 2019; Y. Lee et al., "Negative electrode for lithium metal battery and lithium metal battery comprising the same", U.S. Pat. No. 10,741,846, Aug. 11, 2020) or is otherwise known to those skilled in the art.

3: Competitive analysis

Comparison with first, second, third, sixth, seventh, eighth and tenth patents in the list provided in section 1.2 of this document:
These patents comprise a lithium-containing anode comprising a protective coating comprising 1 layer whereas my invention comprises a lithium-containing anode comprising a protective coating comprising 2 layers.

Comparison with fourth patent (US10777810B2):
Both the fourth patent and my invention comprise a protective coating for a lithium-containing anode that comprises two layers. However, the specified thickness of the second protective layer in the fourth patent is in the range of 1 nm to 100 µm, whereas the specified thickness of the second protective layer in my invention is greater than 101 µm.

Comparison with fifth patent (US10784509B2):
Both the fourth patent and my invention comprise a protective coating for a lithium-containing anode that comprises two layers. However, the specified thickness of the second protective layer in the fourth patent is in the range of 1 nm to 100 µm, whereas the specified thickness of the second protective layer in my invention is greater than 101 µm. Moreover, the material used for the first protective layer in the fifth patent is an electron-conducting material selected from graphene sheets, carbon nanotubes, carbon nanofibers, carbon or graphite fibers, expanded graphite flakes, metal nanowires, conductive polymer fibers, or a combination thereof, whereas my invention uses a polymer matrix with lithium fluoride particles embedded in the matrix.

Comparison with ninth patent (US10347904B2):
Both the fourth patent and my invention comprise a protective coating for a lithium-containing anode that comprises two layers. However, the second (outer) protective coating for this patent comprises a first polymer, a soft segment polymer, and an electrolyte within a crosslinked matrix, whereas certain embodiments of my invention comprises of a second protective layer that does not contain any polymeric or electrolytic material.

4: Appendix

The specific parts of the claim that are being designed around are underlined.

1. US10741846B2:
A negative electrode for a lithium metal battery, the negative electrode comprising:
a lithium metal electrode comprising lithium metal or a lithium metal alloy; and
a protective layer on at least a portion of the lithium metal electrode,
wherein the protective layer has a Young's modulus of about 106 Pascals to about 8 gigaPascals,
wherein the protective layer comprises
<u>a plurality of first particles, wherein a first particle of the plurality of first particles comprises a polymer comprising a styrene unit and has a weight average molecular weight of about 10,000 Daltons to about 500,000 Daltons, and wherein the first particle has a particle size of greater than 1 micrometer to about 100 micrometers,</u>
<u>wherein the polymer comprises homopolystyrene, a poly(styrene-divinylbenzene) copolymer, a poly(styrene-ethylene-butylene-styrene) copolymer, a poly(styrene-methyl methacrylate) copolymer, a poly(styrene-acrylonitrile) copolymer, a poly(styrene-vinylpyridine) copolymer, a poly(acrylonitrile-butadiene-styrene) copolymer, a poly(acrylonitrile-ethylene-propylene-styrene) copolymer, a poly(methyl methacrylate-acrylonitrile-butadiene-styrene) copolymer, a poly((C1-C9 alkyl) methacrylate-butadiene-styrene) copolymer, a poly(styrene-(C1-C9 alkyl) acrylate) copolymer, a poly(acrylonitrile-styrene-(C1-C9alkyl) acrylate) copolymer, or a combination thereof,</u> and
a lithium salt adjacent the first particles, the lithium salt comprising LiSCN, LiN(CN)2, LiClO4, LiBF4, LiAsF6, LiPF6, LiCF3SO3, LiC(CF3SO2)3, LiN(SO2C2F5)2, LiN(SO2CF3)2, LiN(SO2F)2, LiSbF6, LiPF3(CF2CF3)3, LiPF3(CF3)3, LiB(C2O4)2, or a combination thereof, and
<u>a crosslinked material of a polymerizable oligomer comprising an acrylate group, which are disposed between first particles of the plurality of first particles,</u>
<u>wherein the polymerizable oligomer comprises diethylene glycol diacrylate, triethylene glycol diacrylate, tetraethylene glycol diacrylate, polyethylene glycol diacrylate, dipropylene glycol diacrylate, tripropylene glycol diacrylate, ethoxylated trimethylolpropane triacrylate, acrylate-functionalized ethylene oxide, 1,6-hexanediol diacrylate, ethoxylated neopentyl glycol diacrylate; propoxylated neopentyl glycol diacrylate, allyl methacrylate, trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, pentaerythritol triacrylate, ethoxylated propoxylated trimethylolpropane triacrylate propoxylated glyceryl triacrylate, tris(2-hydroxyethyl) isocyanurate triacrylate, pentaerythritol tetraacrylate, dipentaerythritol pentaacrylate, or a combination thereof.</u>

2. US10847799B2:
A negative electrode for a lithium metal battery, the negative electrode comprising:
a lithium metal electrode comprising lithium metal or a lithium metal alloy; and
a protective layer comprising a mixture of a lithium salt and a plurality of organic particles, the protective layer disposed on at least a portion of the lithium metal electrode,

wherein the organic particle comprises a polystyrene homopolymer, a copolymer having a weight average molecular weight of about 10,000 Daltons to about 100,000 Daltons and comprising a styrene repeating unit, or a combination of the polystyrene homopolymer and the copolymer, and wherein the protective layer has a Young's modulus of about 106 pascals to about 1011 pascals, and

wherein the organic particle has a particle size of greater than 1 micrometer to about 100 micrometers.

3. US10608249B2:

A method of making a negative lithium-containing electrode for an electrochemical cell, the method comprising:

depositing a first precursor and a second precursor in a vapor deposition process onto one or more surface regions of a negative electrode material comprising lithium, wherein the first precursor and the second precursor react to form an inorganic-organic composite surface coating on the one or more surface regions, wherein the first precursor comprises an organic mercapto-containing silane and the second precursor comprises an inorganic silane, and the inorganic-organic composite surface coating comprises a first lithium silicate (LixSiOy) moiety, where 0≤x≤4 and 0≤y≤2.

4. US10777810B2:

A lithium metal secondary battery comprising a cathode, an anode, and an electrolyte or an electrolyte/porous separator assembly disposed between said cathode and said anode, wherein said anode comprises:

a) an anode active material layer comprising a layer of lithium or lithium alloy, in a form of a foil, coating, or multiple particles aggregated together, as an anode active material;

b) a first anode-protecting layer having a thickness from 1 nm to 100 μm and comprising a lithium ion-conducting material having a lithium ion conductivity from 10−8 S/cm to 5×10−2 S/cm and being in physical contact with the anode active material layer; and

c) a second anode-protecting layer in physical contact with said first anode-protecting layer, having a thickness from 1 nm to 100 μm and comprising an elastomer having a fully recoverable tensile elastic strain from 2% to 1,000% and a lithium ion conductivity from 10−8 S/cm to 5×10−2 S/cm when measure at room temperature;

wherein said lithium metal secondary battery does not include a lithium-sulfur battery or lithium-selenium battery.

5. US10784509B2:

A lithium metal secondary battery comprising a cathode, an anode, and an electrolyte or an electrolyte/porous separator assembly disposed between said cathode and said anode, wherein said anode comprises:

a) an anode active material layer comprising a layer of lithium or lithium alloy, in a form of a foil, coating, or multiple particles aggregated together, as an anode active material;

b) a first anode-protecting layer having a thickness from 1 nm to 100 μm and comprising a thin layer of electron-conducting material selected from graphene sheets, carbon nanotubes, carbon nanofibers, carbon or graphite fibers, expanded graphite flakes, metal nanowires, conductive polymer fibers, or a combination thereof, wherein said first anode-protecting layer has a specific surface area greater than 50 m2/g and is in physical contact with the anode active material layer; and

c) A second anode-protecting layer in physical contact with said first anode-protecting layer, having a thickness from 1 nm to 100 μm and comprising an elastomer having a fully recoverable tensile elastic strain from 2% to 1,000% and a lithium ion conductivity from 10^{-8} S/cm to 5×10^{-2} S/cm when measure at room temperature;

wherein said lithium metal secondary battery does not include a lithium-sulfur battery or lithium-selenium battery.

6. US10483547B2:

A lithium metal battery comprising:

a lithium metal anode;

a protective layer disposed on the lithium metal anode, the protective layer comprising: i) a polymer and ii) a metal salt comprising a Group 1 or a Group 2 element and a nitrogen-containing additive;

a cathode comprising lithium cobalt oxide, lithium nickel cobalt manganese oxide, lithium nickel cobalt aluminum oxide, lithium iron phosphate, lithium manganese oxide, or a combination thereof; and

a liquid electrolyte disposed between the protective layer and the cathode, the liquid electrolyte comprising an organic solvent,

wherein the metal salt and a nitrogen-containing additive comprising a Group 1 element or Group 2 element are insoluble in the organic solvent of the liquid electrolyte,

wherein the metal salt comprises

at least one selected from a Group 1 element or Group 2 element selected from Cs, Rb, K, Ba, Sr, Ca, and Mg,

$NaNO_3$, or

a combination thereof; and

wherein the nitrogen-containing additive is at least one selected from an inorganic nitrate, an organic nitrate, an inorganic nitrite, an organic nitrite, an organic nitro compound, an organic nitroso compound, an N—O compound, and lithium nitride, and

wherein the metal salt has a solubility of less than 100 parts per million per liter of the organic solvent.

7. US10573933B2:

A lithium metal battery comprising:

a positive electrode;

a negative electrode comprising lithium;

a liquid electrolyte disposed between the positive electrode and the negative electrode; and

an amorphous protective layer disposed on at least a portion of the negative electrode, wherein the protective layer comprises a first polymer selected from at least one of poly(vinyl alcohol) and poly(vinyl alcohol) blend, and a lithium salt,

wherein the protective layer has an elongation of greater than or equal to 100% at a temperature of 25° C.,
wherein the glass transition temperature of polyvinyl alcohol in the amorphous protective layer is in a range of about 40° C. to about 80° C., and
wherein the protective layer has peaks at diffraction angles of about 12.5° 2-theta to about 27.5° 2-theta with a full width at half maximum of 3° to 7° as measured by X-ray diffraction analysis,
wherein a mixed weight ratio of the first polymer to the lithium salt is in a range of about 3:1 to about 3:8, and
wherein a molar ratio of hydroxyl groups of the first polymer to lithium is about 2:1 to about 13:1.

8. US10497927B2:
A method of making a negative electrode for an electrochemical cell that cycles lithium ions, the method comprising:
applying a fluoropolymer via a deposition process to one or more surface regions of an electroactive material selected from the group consisting of: lithium metal, silicon metal, silicon-containing alloys, and combinations thereof, wherein the electroactive material is contained in a pre-fabricated electrode layer and the fluoropolymer reacts with lithium to form a composite surface layer on the one or more surface regions that comprises an organic matrix material having lithium fluoride particles distributed therein and has a thickness greater than or equal to about 5 nm to less than or equal to about 20 nm, and the composite surface layer is formed on at least one surface of the pre-fabricated electrode layer.

9. US10347904B2:
A lithium metal anode comprising:
a lithium metal layer; and
a multi-layer polymer coating over the lithium metal layer, the multi-layer polymer coating comprising:
a first outer polymeric crosslinked gel layer positioned for contact with a battery electrolyte, the first outer polymeric crosslinked gel layer comprising a first polymer, a soft segment polymer, and an electrolyte within a crosslinked matrix; and
a second inner layer disposed between the lithium metal layer and the first outer polymeric crosslinked gel layer and in direct contact with the first outer polymeric crosslinked gel layer, the second inner layer comprising a second polymer providing mechanical strength and a physical barrier to the lithium metal layer.

10. US10770721B2:
A lithium secondary battery comprising a cathode, an anode, and an electrolyte or separator-electrolyte assembly disposed between said cathode and said anode, wherein said anode comprises:
a) a foil or coating of lithium or lithium alloy as an anode active material; and
b) a layer of polymer having a recoverable tensile strain no less than 5%, a lithium ion conductivity no less than 10^{-6} S/cm at room temperature, and a thickness from 1 nm to 10 μm, wherein said polymer contains an ultrahigh molecular weight polymer having a molecular weight from 0.5×10^6 to 9×10^6 grams/mole and is disposed between said lithium or lithium alloy and said electrolyte or

separator-electrolyte assembly, wherein said ultrahigh molecular weight polymer is a thermoplastic and is selected from polyacrylonitrile, polyethylene oxide, polypropylene oxide, polyethylene glycol, polyvinyl alcohol, polyacrylamide, poly(methyl methacrylate), poly(methyl ether acrylate), a copolymer thereof, a sulfonated derivative thereof, a chemical derivative thereof, or a combination thereof.