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(54) **ANODE PROTECTION LAYER**

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None

See application file for complete search history.

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(57) **ABSTRACT**

An electrochemical cell assembly comprising: at least one electrochemical cell or cells comprising—a cathode comprising an electrochemically active material, wherein alkali metal is present in the cathode;—an anode comprising a current collector comprising an electronically conducting, inert metal or non-metal; and said anode further comprising a protection layer containing a first layer and a second layer; wherein the first layer comprises a metal and/or non-metal that alloys with an alkali metal and is formed on the current collecting layer, and an second layer deposited on the first layer, wherein the second layer is an ionically conducting layer having an electronic conductivity of less than 10^{-5} S cm^{-1} ; wherein the cell assembly further comprises a means of applying pressure to the at least one electromechanical cell or cells.

19 Claims, No Drawings

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ANODE PROTECTION LAYER

The present invention relates to an electrochemical cell. The present invention also relates to a method of forming an electrochemical cell, in particular a method of forming a coating on an anode of an electrochemical cell.

BACKGROUND

Electrodes comprising alkali or alkaline earth metals have been used in both primary and secondary electrochemical cells. In particular, alkali metals such as lithium and sodium may be particularly beneficial thanks to the high energy transfer per unit mass that they can provide. Whilst a cell may incorporate lithium or sodium in the anode (i.e. the negative electrode), for example as a lithium or sodium metal or metal alloy foil, various other cell constructions may be employed. For example, a lithium or sodium cell may comprise an anode that does not contain an alkali metal.

Cells comprising alkali metal in the anode, for example in the form of a metal or metal alloy foil, may be subject to the reaction of said alkali metal with the electrolyte, which may form a resistive layer over the anode that may decrease battery performance over time, and may also result in the formation of alkali metal dendrites/mossy deposits during cycling. This can result in short-circuiting and decreased cycling performance. While cells based on alternative anodes (not comprising alkali metal) may not initially suffer from these problems, a layer of alkali metal may nevertheless be formed on the surface of the anode during cycling, as alkali metal is plated on the surface. Dendrites may also be formed. Thus, the performance and/or lifetime of such cells may also be affected.

In view of the above difficulties, the inclusion of a protective layer on the surface of an anode may be desirable. Various protective layers have been proposed. For example, an alloy layer on top of the anode has been suggested as a means of improving the cycling or capacity characteristics of a cell. However, alloy layers comprising alkali metal alloys are highly reducing and may react with the electrolyte over time, resulting in the formation of an ionically resistive layer on top of the electrode. Alkali metal plating on top of the alloy layer may also be observed, along with uneven stripping. Ceramic materials have also been proposed as a candidate for forming a protection layer on an anode. However, the use of a ceramic layer may increase charge transfer resistance of an anode, which may result in inhomogeneous stripping and plating of the alkali metal. The uneven plating and stripping of the alkali metal may then cause localised high current densities and may result in alkali metal deposition on the top of the protective layer. Additionally, the mechanical integrity of the ceramic layer may be compromised due to uneven volume changes.

DESCRIPTION

Before particular examples of the present invention are described, it is to be understood that the present disclosure is not limited to the particular cell, method or material disclosed herein. It is also to be understood that the terminology used herein is used for describing particular examples only and is not intended to be limiting, as the scope of protection will be defined by the claims and equivalents thereof.

In describing and claiming the cell and method of the present invention, the following terminology will be used: the singular forms “a”, “an”, and “the” include plural forms

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unless the context clearly dictates otherwise. Thus, for example, reference to “an anode” includes reference to one or more of such elements.

In accordance with a first aspect of the present invention, there is provided an electrochemical cell assembly comprising:

at least one electrochemical cell or cells comprising
a cathode comprising an electrochemically active material, wherein an alkali metal is present in the cathode;
an anode comprising a current collector comprising an electronically conducting, inert metal or non-metal; and said anode further comprising a protection layer containing a first layer and a second layer; wherein the first layer comprises a metal and/or non-metal that alloys with an alkali metal and is formed on the current collector, and an second layer deposited on the first layer, wherein the second layer is an ionically conducting layer having an electronic conductivity of less than $10^{-5} \text{ S cm}^{-1}$;

wherein the cell assembly further comprises a means of applying pressure to the at least one electrochemical cell or cells.

In accordance with another aspect of the present invention, there is provided an electrochemical cell assembly comprising:

at least one electrochemical cell or cells comprising
a cathode comprising an electrochemically active material, wherein an alkali metal is present in the cathode;
an anode comprising a current collector comprising an electronically conducting, inert metal or non-metal; and said anode further comprising a protection layer containing a first layer and a second layer; wherein the first layer comprises a metal and/or non-metal that alloys with an alkali metal and is formed on the current collector, and an second layer deposited on the first layer, wherein the second layer comprises an ionically conducting layer comprising at least one of a conducting polymer, a ceramic or glass material, a polymer and ceramic composite material; and

wherein the cell assembly further comprises a means of applying pressure to the at least one electrochemical cell or cells.

In accordance with another aspect of the present invention, there is provided a method of forming an electrochemical cell assembly as described above, said method comprising:

- providing a current collector comprising an electronically conducting, inert metal or non-metal;
- contacting at least one metal and/or non-metal that forms an alloy with an alkali metal with the current collector to form a continuous first layer;
- depositing an ionically conducting layer having an electronic conductivity of less than $10^{-5} \text{ S cm}^{-1}$ on the surface of the first layer to form a continuous second layer; wherein steps a) to c) form an anode;
- providing a cathode; wherein steps a) to d) form an electrochemical cell; and applying a means to provide a force to at least one cell in accordance with steps a) to d). As used throughout the specification, the term “anode” refers to the negative electrode in an electrochemical cell, i.e. the electrode at which oxidation occurs during charge of the cell. As used throughout the specification, the term “cathode” refers to the positive electrode in an electrochemical cell, i.e. the electrode at which reduction occurs during charge of the cell.

The protection layer in accordance with the present invention can include two sub-layers. Preferably, the protection

layer comprises a first and second layer, wherein the second layer may be in direct contact with the electrolyte of a cell. Alternatively, the second layer may be in direct contact with the cathode of the cell. Cells may also be envisaged in which the protection layer comprises more than two layers. For example, the protection layer may comprise two or more layers which can alloy with an alkali metal. Additionally or alternatively, the protection layer may comprise two or more ionically conductive layers. Other suitable layers may also be included within the protection layer. Preferably, the protection layer comprises a metal and/or non-metal that alloys with an alkali metal and is formed on the current collector, and a second layer that is deposited on the first layer and comprises an ionically conducting layer having an electronic conductivity of less than $10^{-5} \text{ S cm}^{-1}$.

In forming a protection layer that comprises a first and second layer as described herein, the present inventors have provided a coating that may have beneficial effects on cell performance. Such a protection layer may have improved properties, for example reduced interfacial resistance, in comparison with a cell that comprises a number of different coatings on the anode. In combination, the first and second layers may have a thickness of between 2 nm and 10000 nm, preferably between 10 nm and 4000 nm, more preferably between 100 nm and 5000 nm, for example between 500 nm and 3000 nm. Maintaining a relatively small thickness of the individual layers, and a relatively small thickness of the combination of layers, may reduce or eliminate the tendency of the protective layer to crack. Avoiding or minimising cracking may be beneficial in terms of the lifetime of a cell.

The protection layer or coating in accordance with the present invention may provide an improved battery performance. For example, the electrochemical cell in accordance with the present invention can provide improvements in cycling and capacity life. Without wishing to be bound by any theory, it is believed that the protection layer can reversibly store reactive alkali metals such as lithium and sodium under the protection layer. Following saturation of the alloying layer with alkali metal, further alkali metal may plate under the first layer of the protection layer during cycling of the cell. The protection layer may also allow homogeneous stripping, during discharge, of the alkali metal accumulated under the protection layer. This may be beneficial, as inhomogeneous stripping may have the result of pitting and/or cracking of the alkali metal deposits, which can reduce the lifetime and/or performance of the cell. Inhomogeneous stripping and plating may also result in the formation of alkali metal dendrites, which may cause safety issues and the risk of short circuits, and may lower the energy density of a cell.

While an individual protection layer that allows the formation of an alloy with an alkali metal such as lithium or sodium may be envisaged, significant alkali metal plating may occur on top of the alloying layer alongside the formation of cracking and/or pitting on the surface. The use of a ceramic protection layer alone may also increase charge transfer resistance, while also resulting in inhomogeneous alkali metal stripping and/or plating on the surface. Thus, either an alloying layer alone, or a ceramic protection layer alone, may not be an appropriate means of providing an improved anode structure. The present inventors have surprisingly found that a protection layer having a first and a second layer as defined herein may result in homogeneous stripping of alkali metal deposits formed under the protection layer during cycling. The present inventors have also found that, during charge, alkali metal deposition may occur underneath the alloying layer. Without wishing to be bound

by any theory, this may be a consequence of reduced interfacial resistance in comparison to other protective systems. This could potentially be attributed to the interface between the first and second layer being very dense, meaning that alkali metal nucleation preferentially occurs between the current collector and the alloying layer. The deposition of alkali metal such as lithium underneath the alloying layer may beneficially provide a more even deposition of alkali metal, and provide a smooth anode surface. Deposition of alkali metal under the alloying layer may also prevent chemical side reactions between the alkali metal and the electrolyte. The formation of cracks and voids in the anode surface may also be minimized or prevented. The present inventors have also found reduced impedance of an anode in accordance with the invention when compared with a comparable, unprotected anode. The inventors have also found a reduced impedance in comparison with an anode having either an alloying protection layer alone, or a ceramic protection layer alone. Without wishing to be bound by any theory, it is believed that this reduced impedance may enable deposition/stripping to occur under the protection layer.

The electrochemical cell in accordance with the present invention may be any suitable cell. Preferably, the cell is an all-solid-state cell. Non-limiting examples of suitable electrochemical cells include a lithium or sodium sulphur cell, lithium or sodium ion cell (for example a lithium or sodium NMC cell), or a lithium or sodium air cell. Preferably, the electrochemical cell is a lithium sulphur cell or lithium ion cell. Alternatively, the cell may comprise an alkaline earth metal such as magnesium instead of lithium or sodium. Each electrochemical cell may comprise an anode and a cathode, and an electrolyte present between the anode and the cathode. The second layer of the protection layer may act as an electrolyte, i.e. a solid state electrolyte. In this case, no additional electrolyte may be present. Alternatively, the second layer of the protection layer may act as a solid state electrolyte, with further electrolyte(s) present in the cell. The further electrolyte(s) may be solid and/or liquid.

The electrochemical cell in accordance with the present invention comprises a current collector. This forms part of the anode. The current collector comprises an electronically conducting substrate. Any suitable current collector may be coated with the protective coating described herein. The current collector may comprise an electrically conductive metallic foil, sheet or mesh. A current collector may typically be composed of a metallic conductor that is substantially inert, i.e. the metallic conductor does not participate in reduction or oxidation reactions during cycling of the cell. For example, the current collector may not be formed of an alkali metal such as lithium or sodium. Examples of suitable metals for formation of the current collector include inert metals such as aluminium, copper, nickel, titanium or tungsten. In a preferred example, the current collector comprises copper or nickel, for example copper or nickel foil. The current collector may also comprise a metallic conductor as defined above, wherein the metallic conductor is applied to a substrate, such as a polymer substrate. The substrate may take the form of a polymer such as polyethylene terephthalate (PET). The current collector may have a thickness of between 5 μm and 40 μm , preferably between 10 μm and 25 μm , for example between 15 μm and 20 μm .

The protection layer comprises a first layer on the current collector. Preferably, the first layer is a continuous layer, i.e. covers the whole surface of the current collector. The first layer is in intimate contact with the current collector. The first layer comprises at least one metal and/or non-metal that can form an alloy with an alkali metal such as lithium or

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sodium. The term "alloy" refers to a combination of two or more metals, or a combination of one or more metals with other, non-metallic elements. Examples of suitable alloying metals and non-metals include aluminium, gallium, boron, indium, zinc, carbon, silicon, germanium, tin, lead, antimony, silver, gold, sodium, potassium, magnesium, calcium, and mixtures thereof. Example of base lithium alloys that may be included in the alloy layer include Li_nAl_x , Li_nZn_x , Li_nGa_x , Li_nIn_x , Li_nC_x , Li_nSi_x , Li_nGe_x , Li_nSn_x , Li_nPb_x , Li_nSb_x , Li_nAg_x , Li_nAu_x , Li_nNa_x , Li_nK_x , Li_nMg_x , Li_nCa_x , wherein n may be between 0.1 and 20, for example between 1 and 5, and x may be between 0.5 and 10, for example between 1 and 5. For example lithium-indium alloys that may be formed in the first layer may include $\text{Li}_{0.3}\text{In}_{1.7}$, LiIn , Li_5In_4 , Li_3In_2 , Li_2In and $\text{Li}_{13}\text{In}_3$, but further alloys may additionally/alternatively be formed. One or more base metal alloys may be included in the alloying layer. In a preferred embodiment, the alloying layer comprises a lithium-indium alloy. Alternatively, the alloying layer comprises a lithium-zinc alloy. The alloying layer may comprise a sodium-indium or a sodium-zinc alloy. Alloying of the alloying metal and/or non-metal with alkali metal may occur during cycling of the cell.

The first layer is electronically conductive. The first layer may have an electronic conductivity of greater than $10^{-5} \text{ S cm}^{-1}$, preferably greater than $10^{-3} \text{ S cm}^{-1}$, more preferably greater than $10^{-1} \text{ S cm}^{-1}$, for example greater than 1 S cm^{-1} . The electronic conductivity may also enable alloying reactions to occur between the first layer and alkali metal ions present in the cell, for example in the electrolyte. The electronic conductivity may be measured by a suitable method.

The first layer may have a high alkali metal diffusivity, i.e. allowing the passage of alkali metal ions through the layer. The first layer may have an initial alkali metal diffusivity of greater than $10^{-15} \text{ cm}^2 \text{ s}^{-1}$, preferably greater than $10^{-10} \text{ cm}^2 \text{ s}^{-1}$, more preferably greater than $10^{-8} \text{ cm}^2 \text{ s}^{-1}$, for example greater than $10^{-7} \text{ cm}^2 \text{ s}^{-1}$. The first layer may have a high alkali metal diffusivity in its pristine form, i.e. prior to cycling. Alternatively, the first layer may have a lower alkali metal diffusivity prior to cycling, for example an alkali metal diffusivity lower than $10^{-15} \text{ cm}^2 \text{ s}^{-1}$. During cycling, the alkali metal content within the first layer will vary due to, for example, the point of charge or discharge, and the concentration gradient within the alloying layer will be a function of the charge/discharge. Thus, the alkali metal diffusivity may increase when alkali metal contained in the first layer is stripped during cycling. A high diffusivity of the "intermediate" species (such as alkali metal alloys) that form within the first layer may allow spontaneous and homogeneous stripping of alkali metal formed under the protection layer. This may occur after, for example, the first charge of the cell, when the first layer is lithiated/sodiated and excess lithium/sodium forms a layer between the current collector and the first layer.

The first layer is ionically conducting, i.e. allows the passage of alkali metal ions through the layer. Accordingly, during cell discharge, alkali metal ions can flow through the layer into the solid or liquid electrolyte. Similarly, when the cell is charged, alkali metal ions from the electrolyte can migrate through the coating and deposit beneath the coating as alkali metal, for example lithium or sodium. The first layer may have an ionic conductivity of greater than $10^{-9} \text{ S cm}^{-1}$, preferably greater than $10^{-8} \text{ S cm}^{-1}$, preferably greater than $10^{-7} \text{ S cm}^{-1}$, more preferably greater than $10^{-6} \text{ S cm}^{-1}$, for example greater than $10^{-5} \text{ S cm}^{-1}$. The ionic conductivity may be measured by any suitable method.

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The first layer may have a high ionic conductivity and/or a high alkali metal diffusivity. In one embodiment, the first layer may have an ionic conductivity of greater than $10^{-9} \text{ S cm}^{-1}$ and an alkali metal diffusivity of greater than $10^{-15} \text{ cm}^2 \text{ s}^{-1}$.

The first layer is able to store a certain amount of alkali metal. The amount of alkali metal stored within the first layer varies at different stages in cycling of a cell. The total amount of alkali metal able to be stored within the first layer may be less than 60% of the electrochemical alkali metal storage capacity of the electroactive material within the cathode, preferably less than 30%, preferably less than 10%, for example less than 5%. During charge of the electrochemical cell, the first layer may become saturated with alkali metal. As charging proceeds towards completion, formation (nucleation and growth) of elemental alkali metal beneath the alloying layer may occur.

The thickness of the first layer may be between 1 nm and 5000 nm, preferably between 10 nm and 3000 nm, for example between 100 nm and 1000 nm.

The protection layer further comprises a second layer deposited on the first layer. The second layer is in intimate contact with the first layer. Preferably, the second layer is a continuous layer, i.e. covers the whole surface of the first layer. The second layer may have a uniform thickness. The thickness of the second layer may be between 1 nm and 1000 nm, preferably between 10 nm and 500 nm, for example between 100 nm and 250 nm. The second layer may also act as an electrolyte, as well as performing a protective function on the anode, where the cell is an all-solid-state-cell.

The second layer is ionically conducting, i.e. allows the passage of alkali metal ions through the layer. Accordingly, during cell discharge, alkali metal ions can flow through the coating. Similarly, when the cell is charged, alkali metal ions can migrate through the coating to the alloying layer, under which they may then deposit as alkali metal, for example lithium or sodium. Thus, the second layer can provide a protective function, while allowing passage of alkali metal ions during charge and discharge. The second layer may have an ionic conductivity of greater than $10^{-9} \text{ S cm}^{-1}$, preferably greater than $10^{-8} \text{ S cm}^{-1}$, preferably greater than $10^{-7} \text{ S cm}^{-1}$, more preferably greater than $10^{-6} \text{ S cm}^{-1}$, for example greater than $10^{-5} \text{ S cm}^{-1}$.

The second layer has a low electronic conductivity, i.e. is substantially electronically insulating. The inclusion of a layer with a low electronic conductivity may avoid deposition of alkali metal ions such as Li^+ and Na^+ on top of the protection layer. The low electronic conductivity may also serve to prevent the second layer from effectively working as a further current collector within the cell. The second layer may have an electronic conductivity of less than $10^{-5} \text{ S cm}^{-1}$, preferably less than $10^{-8} \text{ S cm}^{-1}$, more preferably less than $10^{-10} \text{ S cm}^{-1}$. In one example the electronic conductivity is less than $10^{-12} \text{ S cm}^{-1}$.

The second layer may comprise at least one of a ceramic or glass material, a polymer material, a polymer and ceramic composite material, and combinations thereof. Suitable ceramic or glass materials include, for example, one or more elements selected from lithium, sodium, magnesium, oxygen, phosphorous, nitrogen, silicon, germanium, titanium, zirconium, tin, aluminium, sulfur, boron, selenium, fluorine, chlorine, bromine or iodine. Suitable ceramic materials may be stoichiometric or non-stoichiometric. The ceramic material may be an oxynitride, sulphide, phosphate, oxide, oxysulfide, thiophosphate, borate, oxyborate, borohydride, silicate, aluminate or thioaluminate compound, or a combination thereof. Examples of suitable materials include

lithium oxynitride, lithium sulphide, lithium phosphate, lithium oxide, lithium oxysulfide, lithium thiophosphate, lithium borate, lithium oxyborate, lithium borohydride, lithium silicate, lithium aluminate and lithium thioaluminate, or combinations thereof. Alternatively, the material may be selected from one or more of sodium oxynitride, sodium sulphide, sodium phosphate, sodium oxide, sodium oxysulfide, sodium thiophosphate, sodium borate, sodium oxyborate, sodium borohydride, sodium silicate, sodium aluminate and sodium thioaluminate. The ceramic material may be an amorphous material.

Examples of suitable ceramic materials include LiPON, LLZO, LATP, LGPS, LPS and LAGP. LiPON, LLZO, LATP, LGPS, LPS and LAGP are examples of materials that are also useful as solid-state conductive electrolytes. Further examples of conductive ceramic or glass materials include $\text{Li}_2\text{S}-\text{P}_2\text{S}_5-\text{LiI}$, $\text{Li}_2\text{S}-\text{SiS}_2-\text{LiI}$, $\text{Li}_2\text{S}-\text{SiS}_2-\text{Li}_3\text{PO}_4$, $\text{Li}_2\text{O}-\text{P}_2\text{O}_5-\text{Li}_2\text{SO}_4$, $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{LiI}$, $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3$, $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$, and $\text{Li}_2\text{O}-\text{SiO}_2-\text{B}_2\text{O}_3$.

A particularly preferred ceramic material is a lithium oxynitride, such as a lithium phosphorus oxynitride. LiPON is an example of an amorphous, non-stoichiometric lithium phosphorus oxynitride that has a low electronic conductivity and a high ionic conductivity. Exemplary values of electronic conductivity and ionic conductivity for LiPON are in the region of $10^{-12} \text{ S cm}^{-1}$ and $10^{-6} \text{ S cm}^{-1}$ respectively.

The second layer may comprise a conductive polymer material, for example an ionically conductive polymer. Additionally or alternatively, the second layer may comprise a polymer material having an alkali metal salt distributed within the polymer material. This may provide or increase ionic conductivity within the polymer. The second layer may instead or additionally comprise a polymer-ceramic composite material. A polymer-ceramic composite material may comprise ceramic particles that are bound together by at least one polymer material. The polymer or polymers used to form the polymer-ceramic composite material may have inherent alkali metal ion conductivity, or may be mixed with alkali metal salts.

For example, the polymer material may comprise a lithium salt (e.g. LiTFSI) dissolved within a polymer phase, for example polyethylene oxide. Further examples of lithium salts include lithium hexafluorophosphate, lithium hexafluoroarsenate, lithium nitrate, lithium perchlorate, lithium trifluoromethanesulfonimide, lithium bis(oxalate) borate and lithium trifluoromethanesulphonate. Suitable sodium salts include sodium hexafluorophosphate, sodium hexafluoroarsenate, sodium nitrate, sodium perchlorate, sodium trifluoromethanesulfonimide, sodium bis(oxalate) borate and sodium trifluoromethanesulphonate. Combinations of salts may be employed.

The polymer may comprise at least one functional group selected from the list of amine, amide, carbonyl, carboxyl, ether, thioether and hydroxyl groups, and mixtures thereof. Non-limiting examples of polymers include polyanhydrides, polyketones, polyesters, polystyrenes, polyamides, polyimides, polyurethanes, polyolefins, polyvinyls. Non-limiting examples of ionically conductive polymers may include nitrogen or sulfur containing polymers, for example polypyrroles (PPY), polycarbazoles, polyindoles, polyazepines, polyanilines, polythiophenes, PEDOT, PPS. Further examples of ionically conductive polymers may include poly(fluorene)s, polyphenylenes, polypyrenes, polyazulenes, polynaphthalenes, poly(acetylene)s (PAC) and poly(p-phenylene vinylene) (PPV). In a preferred embodiment, the polymer material is polyethylene oxide.

The current collector may be used to assemble any suitable cell. The anode may be coupled to any suitable cathode comprising positive electrode material. For example, the current collector and a cathode comprising a mixture of electroactive material and solid electroconductive material may be placed in contact with an electrolyte. The electrolyte may be a solid or liquid electrolyte and may be located between the second layer of the protection layer and the cathode. Alternatively, the second layer of the protection layer may itself act as an electrolyte and no additional electrolyte may be present.

The cathode of the electrochemical cell includes a suitable electroactive material, such as an electroactive sulphur material. The cathode may be ionically conductive, i.e. it can enable conduction of ions (i.e. alkali cations, Li^+ or Na^+) in the solid-state. The cathode comprises an alkali metal, such as lithium or sodium, such that the lithiated or sodiated cathode may provide a source of alkali metal ions during cycling of the cell. Examples of positive electroactive materials suitable for lithium-based cells include composite materials which comprise lithium sulfide, sulfur, lithium oxide, oxygen, lithium cobalt oxide, lithium nickel cobalt manganese oxides, lithium nickel aluminium oxides, lithium nickel cobalt aluminium oxides, lithium nickel manganese oxides, lithium manganese oxides, lithium iron phosphate, lithium manganese phosphate, lithium cobalt phosphate, lithium iron fluoride, and combinations thereof. Examples of positive electroactive materials suitable for sodium-based cells include composite materials which comprise sodium cobalt oxides, sodium vanadium oxides, sodium manganese oxides, sodium nickel cobalt manganese oxides, sodium chromium oxides, sodium iron phosphate, sodium vanadyl fluorophosphates, sodium iron fluorides, and combinations thereof.

Where the cathode includes an electroactive sulphur material, this may comprise elemental sulfur, sulfur-based organic compounds, sulfur-based inorganic compounds and sulfur-containing polymers. Preferably, elemental sulfur or Li_2S is used. In one embodiment, the cathode comprises a sulfur-carbon composite. The cathode may comprise an electroactive sulfur material that may also be ionically conductive. This material may contain sulfur as well as additional elements such as Li, Na, Mg, P, N, Si, Ge, Ti, Zr, Sn, B, Al, F, Cl, Br, I, O or any combination thereof. Examples of sulfur containing materials that are also ionically conductive include LGPS, Li_3PS_4 or $\text{Li}_7\text{P}_3\text{S}_{11}$. In one embodiment, the cathode may comprise a sulfur-carbon composite that is also ionically conductive.

The cathode may further comprise a solid electroconductive material. The solid electroconductive material may be any suitable conductive material. Preferably, this solid electroconductive material may be formed of carbon. Examples include carbon black, carbon fibre, graphene, reduced graphene oxide and carbon nanotubes. Other suitable materials include metal (e.g. flakes, filings and powders) and conductive polymers. Examples of conductive polymers include polypyrrole, polythiophene, polyaniline, polyacetylene, polyphenylene vinylene and poly(3,4-ethylenedioxythiophene). Preferably, carbon black is employed. In one embodiment, where the cathode comprises a sulfur-carbon composite, a further solid electroconductive material may be absent from the cathode.

The cathode may further comprise an ionically conductive material, specifically a solid Li^+ or Na^+ ionic conductor. The ionically conductive material may have a bulk ionic conductivity of greater than 10^{-7} S/cm at 25°C ., for example greater than 10^{-6} S/cm . Where the cathode contains an

electroactive, ionically conductive material such as Li_3PS_4 or $\text{Li}_x\text{P}_y\text{S}_z$, a further ionically conductive material may be absent. In some examples, the lithium-ion conductive material comprises a ceramic material. The ceramic material may have a crystalline, polycrystalline, partially crystalline, or amorphous structure. Suitable ceramic materials include, but are not limited to, oxides, carbonates, nitrides, carbides, sulfides, oxysulfides, and/or oxynitrides of metals and/or metalloids. In some cases, the ceramic material comprises lithium. Non-limiting examples of suitable solid-state electrolytes of sufficient ionic conductivity may be produced by a combination of various lithium compounds, such as ceramic materials including lithium include lithium oxides (e.g., Li_2O , LiO , LiO_2 , LiRO_2 , where R is scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and/or lutetium), lithium carbonate (Li_2CO_3), lithium nitrides (e.g., Li_3N), lithium oxysulfide, lithium oxynitride, lithium garnet-type oxides (e.g., $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$), $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, lithium phosphorus oxynitride, lithium silicosulfide, lithium germanosulfide, lithium lanthanum oxides, lithium titanium oxides, lithium borosulfide, lithium aluminosulfide, lithium phosphosulfide, lithium silicate, lithium borate, lithium aluminate, lithium phosphate, lithium halides, and combinations of the above. In certain cases, the ceramic material comprises a lithium oxide, a lithium nitride, or a lithium oxysulfide. In some embodiments, the ceramic includes a carbonate and/or a carbide. In a sodium-based cell, the sodium ion equivalent of any of these materials may be used.

In some embodiments, the lithium-ion-conductive material may be selected from species that can donate electron pairs (e.g., a Lewis base). Examples of suitable electron-donating materials include, but are not limited to, lithium oxides (e.g., Li_2O , LiO , LiO_2 , LiRO_2 , where R is scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and/or lutetium), lithium carbonate (Li_2CO_3), lithium nitrides (e.g., Li_3N), lithium oxysulfide, lithium oxynitride, lithium garnet-type oxides (e.g., $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$), $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, lithium phosphorus oxynitride, lithium silicosulfide, lithium germanosulfide, lithium lanthanum oxides, lithium titanium oxides, lithium borosulfide, lithium aluminosulfide, lithium phosphosulfide, lithium silicate, lithium borate, lithium aluminate, lithium phosphate, lithium halides, and combinations of the above. Sodium equivalents of the above may also be used.

Examples of ceramic materials that can be used as the lithium-ion conductive material include: Li-containing oxides e.g. $\text{Li}_{3.3}\text{La}_{0.56}\text{TiO}_3$; Nasicon structure (eg: $\text{LiTi}(\text{PO}_4)_3$); LiSICON ($\text{Li}_{1.4}\text{Zn}(\text{GeO}_4)_4$); $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$; Garnet: $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$; Li_2O ; other oxides e.g. Al_2O_3 , TiO_2 , ZrO_2 , SiO_2 , ZnO ; sulfides e.g. Li_2S — P_2S_5 ; antiperovskites e.g. Li_3OCl ; hydrides e.g. LiBH_4 , LiBH_4 — LiX ($\text{X}=\text{Cl}$, Br , I), LiNH , LiNH_2 , Li_3AlH_6 , Li_2NH ; borates or phosphates e.g. $\text{Li}_2\text{B}_4\text{O}_7$, Li_3PO_4 , LiPON ; carbonates or hydroxides e.g. Li_2CO_3 , LiOH ; fluorides, e.g. LiF ; nitrides e.g. Li_3N ; sulfides e.g. lithium borosulfides, lithium phosphosulfides, lithium aluminosulfides, oxysulfides, praseodymium oxide. At least one of said ceramic materials may be used, or combinations thereof. In a sodium sulphur cell, the sodium ion equivalent of any of these conductive materials may be utilised.

In some examples, the lithium-ion conductive material may be formed of a polymeric material which is inherently ionically conductive, e.g. Nafion. Alternatively, polymers

blended with lithium (or sodium) salts, which can achieve bulk conductivities of greater than 10^{-7} S/cm, may also be used. Examples of suitable polymers include EO based polymers (for example PEO); acrylate based polymer (for example PMMA); polyamines (polyethyleneimine); siloxanes (poly(dimethylsiloxane)); polyheteroaromatic compounds (e.g., polybenzimidazole); polyamides (e.g. Nylons), polyimides (e.g. Kapton); polyvinyls (e.g. polyacrylamide, poly(2-vinyl pyridine), poly(N-vinylpyrrolidone), poly(methylcyanoacrylate), poly(vinyl acetate), poly(vinyl alcohol), poly(vinyl chloride), poly(vinyl fluoride); inorganic polymers (e.g. polysilane, polysilazane, polyphosphazene, polyphosphonate); polyurethanes; polyolefins (e.g. polypropylene, polytetrafluoroethylene); polyesters (e.g. polycarbonate, polybutylene terephthalate). In one embodiment, co-block polymers such as Nafion may be used. At least one of said polymeric materials may be used, or combinations thereof. In one embodiment, the cathode contains ceramic particles in combination with one or more ionically conductive polymers.

The cathode may additionally include a binder for binding the cathode components together, for example PEO.

Optionally, the cathode may also comprise a current collector comprising an electrically conductive material, for example a metal such as aluminium.

Where an additional electrolyte is present, any suitable electrolyte may be included within the electrochemical cell. In one embodiment, the electrolyte is a liquid electrolyte. The electrolyte may comprise an organic solvent and an electrolyte salt. Suitable organic solvents include ethers, esters, amide, amine, sulfoxides, sulfamides, organophosphates, ionic liquids, carbonates and sulfones. Mixtures of one or more solvents may be employed. Examples of solvents include ethylene carbonate, dimethyl carbonate, tetrahydrofuran, 2-methyltetrahydrofuran, methylpropylpropionate, ethylpropylpropionate, methyl acetate, 1,2-dimethoxyethane, 1,3-dioxolane, diglyme (2-methoxyethyl ether), triglyme, tetraglyme, butyrolactone, 1,4-dioxane, 1,3-dioxane, hexamethyl phosphoamide, pyridine, dimethyl sulfoxide, tributyl phosphate, trimethyl phosphate, N, N, N, N-tetraethyl sulfamide, and sulfones and mixtures thereof.

Alternatively, for example in the case of an all-solid-state cell, the electrolyte of the cell may be a solid electrolyte, for example a solid-state polymer or ceramic electrolyte. The solid electrolyte may comprise at least one of a ceramic or glass material, a polymer material, a polymer and ceramic composite material, and combinations thereof. The second layer of the protective layer may act as the electrolyte and, in this case, no separate electrolyte may be present. Alternatively, a further electrolyte may be present. The further electrolyte may be a solid electrolyte, or a liquid electrolyte as described above.

Suitable ceramic or glass materials include, for example, one or more elements selected from lithium, oxygen, phosphorous, nitrogen, sulfur, boron, selenium, fluorine, chlorine, bromine or iodine. Suitable ceramic materials may be stoichiometric or non-stoichiometric. The ceramic material may be an oxynitride, sulphide, phosphate, oxide, oxysulfide, thiophosphate, borate, oxyborate, borohydride, silicate, aluminate or thioaluminate compound, or a combination thereof. Examples of suitable materials include lithium oxynitride, lithium sulphide, lithium phosphate, lithium oxide, lithium oxysulfide, lithium thiophosphate, lithium borate, lithium oxyborate, lithium borohydride, lithium silicate, lithium aluminate and lithium thioaluminate, or combinations thereof. Alternatively, the material may be selected from one or more of sodium oxynitride, sodium sulphide,

sodium phosphate, sodium oxide, sodium oxysulfide, sodium thiophosphate, sodium borate, sodium oxyborate, sodium borohydride, sodium silicate, sodium aluminate and sodium thioaluminate. The ceramic material may be an amorphous material.

Examples of suitable ceramic materials include LiPON, LLZO, LATP, LGPS, LPS and LAGP. LiPON, LLZO, LATP, LGPS, LPS and LAGP are examples of materials that are also useful as solid-state conductive electrolytes. Further examples of conductive ceramic or glass materials include $\text{Li}_2\text{S}-\text{P}_2\text{S}_5-\text{LiI}$, $\text{Li}_2\text{S}-\text{SiS}_2-\text{LiI}$, $\text{Li}_2\text{S}-\text{SiS}_2-\text{Li}_3\text{PO}_4$, $\text{Li}_2\text{O}-\text{P}_2\text{O}_5-\text{Li}_2\text{SO}_4$, $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{LiI}$, $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3$, $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$, and $\text{Li}_2\text{O}-\text{SiO}_2-\text{B}_2\text{O}_3$.

A particularly preferred ceramic material is a lithium oxynitride, such as a lithium phosphorus oxynitride. LiPON is an example of an amorphous, non-stoichiometric lithium phosphorus oxynitride that has a low electronic conductivity and a high ionic conductivity. Exemplary values of electronic conductivity and ionic conductivity for LiPON are in the region of $10^{-12} \text{ S cm}^{-1}$ and $10^{-6} \text{ S cm}^{-1}$ respectively.

The electrolyte may comprise a conductive polymer material, for example an ionically conductive polymer. Additionally or alternatively, the electrolyte may comprise a polymer material having an alkali metal salt distributed within the polymer material. This may provide or increase ionic conductivity within the polymer. The electrolyte may instead or additionally comprise a polymer-ceramic composite material. A polymer-ceramic composite material may comprise ceramic particles that are bound together by at least one polymer material. The polymer or polymers used to form the polymer-ceramic composite material may be mixed with alkali metal salts.

Suitable alkali metal salts for inclusion in the electrolyte include lithium or sodium salts. Suitable lithium salts include lithium hexafluorophosphate, lithium hexafluoroarsenate, lithium nitrate, lithium perchlorate, lithium trifluoromethanesulfonimide, lithium bis(oxalate) borate and lithium trifluoromethanesulphonate. Suitable sodium salts include sodium hexafluorophosphate, sodium hexafluoroarsenate, sodium nitrate, sodium perchlorate, sodium trifluoromethanesulfonimide, sodium bis(oxalate) borate and sodium trifluoromethanesulphonate. Preferably the lithium salt is lithium trifluoromethanesulphonate (also known as lithium triflate). Combinations of salts may be employed. For example, lithium triflate may be used in combination with lithium nitrate. The lithium salt may be present in the electrolyte at a concentration of 0.1 to 6 M, preferably, 0.5 to 3 M, for example, 1 M.

The electrolyte may also comprise lithium or sodium polysulphides. For example, lithium polysulphides may be added to the electrolyte before the cell is discharged. The concentration of lithium polysulphide dissolved in the electrolyte may be between 0.1% and 20% weight % (preferred concentration 1.5%). Examples of suitable lithium polysulphides include Li_2S_n , where $n \geq 5$, for example, 6 to 15, for example, 8-12 (e.g. 8). Lithium or sodium polysulphides may help to buffer the electrolyte, increase capacity of the cell or act as a source of sulphur to compensate for any loss of sulphur through the formation of non-conducting species.

A cell in accordance with the present invention may be provided in a suitable housing. This housing can define the electrochemical zone. Preferably, the housing is flexible, for example a flexible pouch. The pouch may be formed of a composite material, for example a metal and polymer composite. In one embodiment, one or more cells is enclosed in the housing. The cell or cells may be sealed in the pouch. A

region of each of the cell or cells may protrude from the housing. This region may be coupled to a contact tab formed of, for example, nickel. The contact tab may be connected to the alkali metal or alkali metal alloy by any suitable method, for example by (ultrasonic) welding. Alternatively, the contact tab itself may protrude from the housing. Where a plurality of electrochemical cells are present in the cell assembly, a region of each of the anodes may be pressed or coupled together to form a pile of anodes that may be connected to a contact tab.

A cell in accordance with the present invention may be subjected to a force. Preferably, the force is an anisotropic force i.e. has a different value when measured in different directions. A component of the force is applied, for example is normal to, an active surface of the anode of the electrochemical cell. In one embodiment, the force is applied continuously to the cell. In one embodiment, the force is maintained at a particular value. Alternatively, the force may vary over time. The force may be applied across the entire surface of the anode. Alternatively, the force may be applied over a portion of the surface of the anode, such as over at least 80% of the surface, preferably over at least 60%, preferably over at least 40% of the surface, for example over at least 20% of the surface. The force may be applied directly to the cell. Alternatively, the force may be applied to one or more plates, for example metal plates, that are situated outside of the cell. The force may be applied externally to the housing in which one or more cells is contained. For example, one or more cells may be contained within a flexible pouch, and a force may be applied externally to the flexible pouch.

The force may enhance the performance of an electrochemical cell. Without wishing to be bound by any theory, it is believed that the pressure applied to the anode enables intimate contact to be maintained between the protection layer and the alkali metal or metal alloy layer. The application of pressure to the anode may enable formation of alkali metal plating below the protection layer, between the protection layer and the alkali metal/metal alloy. This may avoid or reduce the formation of plating on top of the protection layer, which may be inhomogeneous and may result in cracking or pitting on the surface. Where plating occurs under the protection layer, the smooth surface of the anode may be preserved, and the formation of cracks or voids on the surface may be reduced. Dendrite formation may then be prevented. Furthermore, alkali metal depositions located under the protection layer are not in direct contact with the electrolyte. This may prevent the electrolyte from being reduced during cycling, which may avoid a reduction in cycle life of a cell.

In one embodiment, the force may be a clamping force. Alternatively, the force may be a compression force. The clamping force may be applied to the cell using a clamp. Alternatively, one or more constricting elements may be positioned around the exterior of the cell or cells. The constricting element may take the form of a band or tubing that surrounds at least part of the exterior of the cell or cells. The band may be made of any suitable material. In one embodiment, the band is formed of an elastic material that may be stretched around the cell or cells and, when in position, applies a constricting force. In one embodiment, the band is an elastic band. Alternatively, the band may be tightened around the cell or cells. The constricting element may also take the form of a shrink wrap material. In a further arrangement, one or more compression springs may be used, for example the cell or cells may be contained within a containment structure in which one or more compression

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springs are located between the containment structure and the cell. Other means of applying force can include screws or weights.

One or more of the above methods of applying a force may be employed. Any suitable force of greater than 0 MPa may be used. The force applied to the cell or cells may be within the range of up to 0.5 MPa, preferably up to 2 MPa, for example up to 5 MPa. The force may be at least 0.1 MPa, preferably at least 0.5 MPa, for example at least 1 MPa. The force may be between 0.1 MPa and 5 MPa, preferably between 0.5 MPa and 3 MPa, for example between 1 MPa and 1.5 MPa.

Also disclosed herein is a method for forming an electrochemical cell comprising a protection layer as described above. In particular, the protection layer may comprise a metal and/or non-metal that alloys with an alkali metal and is formed on a current collector, and a second layer deposited on the first layer and comprises an ionically conducting layer having an electronic conductivity of less than 10^{-5} S cm^{-1} . In accordance with one aspect of the present invention, there is provided a method of forming an electrochemical cell assembly as described above, said method comprising a) providing a current collector; b) contacting at least one metal and/or non-metal that forms an alloy with an alkali metal with the current collector to form a continuous first layer, c) depositing an ionically conducting layer having an electronic conductivity of less than 10^{-5} S cm^{-1} on the surface of the first layer to form a continuous second layer, and providing a cathode, wherein steps a) to d) form an electrochemical cell; and applying a means to provide a force to at least one cell formed in accordance with steps a) to d). Preferably, at least one of the first and second layers is a continuous layer, and more preferably both the first and second layers are continuous.

Any suitable method may be used to form the first layer. Examples of suitable methods include physical or chemical deposition methods, such as physical or chemical vapour deposition. Suitable methods may include plasma-enhanced chemical vapour deposition, sputtering, evaporation, electron-beam evaporation, and chemical vapor deposition (CVD). These methods may be used, for example, to deposit a first layer on the current collecting layer. Additionally or alternatively, these methods may be used to deposit the second layer of the protection layer onto the first layer. Alternative methods of forming the first and/or second layers may include ink-jet printing, slot die and spray coating. These methods may be used for the application of, for example, a second layer comprising a polymer.

Throughout the description and claims of this specification, the words "comprise" and "contain" and variations of them mean "including but not limited to", and they are not intended to (and do not) exclude other moieties, additives, components, integers or steps. Throughout the description and claims of this specification, the singular encompasses the plural unless the context otherwise requires. In particular, where the indefinite article is used, the specification is to be understood as contemplating plurality as well as singularity, unless the context requires otherwise.

Features, integers, characteristics, compounds, chemical moieties or groups described in conjunction with a particular aspect, embodiment or example of the invention are to be understood to be applicable to any other aspect, embodiment or example described herein unless incompatible therewith. All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at

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least some of such features and/or steps are mutually exclusive. The invention is not restricted to the details of any foregoing embodiments. The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

The invention claimed is:

1. An electrochemical cell assembly comprising:

at least one electrochemical cell or cells comprising

a cathode comprising an electrochemically active material, wherein alkali metal is present in the cathode; an anode comprising a current collector comprising an electronically conducting, inert metal or non-metal; and said anode further comprising a protection layer containing a first layer and a second layer, wherein the first layer comprises a metal and/or non-metal that is able to alloy with an alkali metal and is positioned on the current collector, and the second layer is a ceramic layer that is deposited on the first layer, wherein the second layer is an ionically conducting layer having an electronic conductivity of less than 10^{-5} S cm^{-1} ;

wherein the cell assembly is further configured to apply pressure continuously to the at least one electrochemical cell or cells, and

wherein a total amount of alkali metal able to be stored within the first layer is less than 60% of an electrochemical alkali metal storage capacity of the electrochemically active material within the cathode.

2. The electrochemical cell assembly of claim 1, wherein the cell further comprises an electrolyte.

3. The electrochemical cell assembly of claim 2, wherein the electrolyte is a liquid electrolyte.

4. The electrochemical cell assembly of claim 3, wherein the liquid electrolyte contains an alkali metal salt at a concentration above 75% of its saturation concentration.

5. The electrochemical cell assembly as claimed in claim 1, wherein the first layer comprises at least one metal or non-metal selected from aluminium, boron, zinc, gallium, indium, carbon, silicon, germanium, tin, lead, antimony, silver, gold, sodium, potassium, magnesium, calcium, and mixtures thereof.

6. The electrochemical cell assembly as claimed in claim 1, wherein the first layer has an electronic conductivity of more than 10^{-5} S cm^{-1} .

7. The electrochemical cell assembly as claimed in claim 1, wherein the first layer has a lithium diffusivity, during cycling, of more than 10^{-5} S cm^{-1} .

8. The electrochemical cell assembly as claimed in claim 1, wherein the first layer has an ionic conductivity of greater than 10^{-9} S cm^{-1} .

9. The electrochemical cell assembly as claimed in claim 1 wherein the first layer has a thickness of between 1 nm to 5000 nm.

10. The electrochemical cell assembly as claimed in claim 1, wherein the second layer comprises an oxynitride, sulphide, phosphate, oxide, oxysulfide, thiophosphate, borate, oxyborate, borohydride, silicate, aluminate, or thioaluminate compound, or a combination thereof.

11. The electrochemical cell assembly as claimed in claim 10, wherein the ceramic material is LIPON.

12. The electrochemical cell assembly as claimed in claim 1, wherein the second layer has an ionic conductivity of greater than 10^{-9} S cm^{-1} .

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13. The electrochemical cell assembly as claimed in claim 1, wherein the second layer has a thickness of between 1 nm and 1000 nm.

14. The electrochemical cell assembly as claimed in claim 1, wherein the means of applying a force comprises a band, wrap or tubing positioned on the outside of the cell. 5

15. The electrochemical cell assembly as claimed in claim 1, wherein the current collector comprises nickel or copper.

16. The electrochemical cell assembly as claimed in claim 1, wherein the total amount of alkali metal able to be stored within the first layer is less than 30% of the electrochemical alkali metal storage capacity of the electroactive material within the cathode. 10

17. The electrochemical cell assembly as claimed in claim 1, wherein the cell or cells are selected from a lithium sulphur cell, sodium sulphur cell, lithium ion cell, sodium ion cell, lithium air cell or sodium air cell. 15

18. A method of forming an electrochemical cell assembly in accordance with claim 1, said method comprising the steps of:

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a) providing a current collector;

b) contacting at least one metal and/or non-metal that is able to form an alloy with an alkali metal with the current collector to form a continuous first layer;

c) depositing an ionically conducting layer having an electronic conductivity of less than 10^{-5} S cm⁻¹ on the surface of the first layer to form a continuous second layer; wherein steps a) to c) form an anode;

d) providing a cathode; wherein steps a) to d) form an electrochemical cell;

e) pressure to at least one cell in accordance with steps a) to d), thereby resulting in the electrochemical cell assembly.

19. The method as claimed in claim 18, wherein at least one of the first and second layers is formed by physical vapour deposition.

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