A Film Material And A Process Of Preparing The Same

References to Related Applications

This application claims priority to Singapore application number 10201808331W filed on 24 September 2018, the disclosure of which is hereby incorporated by reference.

Technical Field

The present invention relates to a film material and a process of preparing the same for stable sodium metal anodes at room temperature.

Background Art

The sodium metal battery was first developed in 1966 at Ford Motor Company. The deployed version of sodium metal battery exists in the high-temperature form (~350°C) (grid energy storage), it is susceptible to catch fire, and not suitable for mobile applications, e.g., electric vehicles.

The room temperature version of sodium metal battery is difficult to realize due to poor stability of solid-electrolyte interphase (SEI) and sodium dendrite formation which may readily cause short-circuit of the cell.

An interphase is a thin region where two distinct chemical phases stabilize themselves, and it can be developed intrinsically or extrinsically (artificial interphase) over a parent phase (bulk phase). The intrinsic interphase grows itself and it is found to be less effective in preserving the integrity of the bulk phase. The properties of an intrinsic interphase are largely controlled by the intrinsic parameters, for instance, chemical potential or redox potential, which are complex and offer limited room to alter.

Modification of the anode and formation of ex-situ/in-situ interphases have been investigated to stabilize metal anode (at moderate currents). An ideal artificial interphase must be transparent enough to incoming ions, while it must be sufficiently opaque to the particles on the bulk phase. The artificial interphases developed hitherto comprise a single chemical component (mono-phasic interphase), which is effective in stabilizing sodium metal anode at low currents (<1 mA/cm2), while at high current rates, the stability is observed to be compromised.

Therefore, there is a need to provide a process and an interphase film for sodium metal anodes that overcome or ameliorate one or more of the disadvantages mentioned above.

Summary

~~In one aspect, the~~The present disclosure relates to a film material comprising a combination of a metal amide with a metal oxide, or a combination of a metal halide with a metal alloy, wherein said metal is selected from Group I of the Periodic Table of Elements.

In one aspect, the present disclosure relates to a film material comprising a combination of a metal halide with a metal alloy, wherein said metal is selected from Group I of the Periodic Table of Elements.

Advantageously, the film material can prevent dendrite formation and short-circuiting of an electrochemical cell. The combination of the at least two metal compounds is important as a film material comprising a single component (such as sodium oxide Na_2O alone) may not be able to stabilize sodium metal anodes at room temperature.

~~In another aspect, the~~The present disclosure relates to a process of preparing a film material comprising the step of contacting a solid phase material and a vapor phase material,

wherein the solid phase material is a metal selected from Group 1 of the Periodic Table, and

wherein the vapor phase material comprises a combination of an amide precursor with an oxide precursor, or a combination of a metal halide precursor and a metalloid halide precursor.

In another aspect, the present disclosure relates to a process of preparing a film material comprising the step of

contacting a solid phase material and a vapor phase material,

wherein the solid phase material is a metal selected from Group 1 of the Periodic Table,

wherein the vapor phase material comprises a combination of a metal halide precursor and a metalloid halide precursor.

Advantageously, the *ex situ* film material formed in the present disclosure can be developed without electrochemical treatment or any other additional process and with good control of film thickness. The attributes of the film material do not depend on the intrinsic parameters, and hence can be tuned to a great extent. On the other hand, other dissolved strategies offer little control on the physical and chemical properties and are more difficult to realize.

Further advantageously, the growth rate of the film material is in the range of 0.1 to 1 µm/s, which is much faster than other growth processes, such as atomic layer deposition (ALD). Even though slow growth process can offer good control over the film thickness, it may affect the integrity of sodium metal electrode. Alkali metal, in particular sodium metal, degrades quickly even in an inert gas atmosphere, therefore the interphase developed using a slow process might affect integrity of the sodium metal electrode.

In another aspect, the present disclosure relates to an interphase protected sodium metal anode, wherein said interphase is a film material as defined herein.

Advantageously, direct formation of the artificial interphase on sodium metal anode using ammonia vapor can offer great control of the electrode roughness and avoid the use of liquid ammonia which can readily dissolve the sodium metal.

Further advantageously, the sodium metal anode can be stabilized at room temperature as compared to other film protected anodes which require a higher temperature to function.

In another aspect, the present disclosure relates to an electrochemical cell comprising the sodium metal anode as defined herein.

Advantageously, the electrochemical cell exhibits ultra-long cycle life at relatively high current densities. The interphase film helps the electrochemical cell to endure at practical current densities and has the potential to survive at high capacity loads.

Definitions

The following words and terms used herein shall have the meaning indicated:

The term “stable”, “stability” and grammatical variants thereof, in the contexts of this specification, refers to an electrode that can be operated with no sign of short circuiting and sudden increase of voltage or current.

The term “interphase” as used herein refers to a thin region where two distinct chemical phases stabilize themselves.

The term “extrinsically” as used herein refers to the preparation process of a film that is grown artificially to form an *ex situ* interphase.

The term “volatile” as used herein refers to a property of a substance, which can be used to describe how easily the substance vaporizes from a liquid phase or a solid phase to a gaseous phase at a given temperature and pressure. In general, a substance having a high vapour pressure may indicate a high volatility while a substance with a high boiling point can indicate low volatility.

Claims

1. A film material comprising ~~a combination of a metal amide with a metal oxide, or~~ a combination of a metal halide with a metal alloy, wherein said metal is selected from Group I of the Periodic Table of Elements.

2. The film material of claim 1, wherein said metal is selected from the group consisting of lithium, sodium, and potassium.

3. The film material of claim 1 or 2, wherein said metal halide is selected from the group consisting of metal fluoride, metal chloride, metal bromide and metal iodide.

4. The film material of any one of claims 1 to 3, wherein said metal alloy further comprises an element selected from the group consisting of a transition metal, a Group 14 metal and a Group 14 metalloid.

5. The film material of any one of claims 1 to 4, which is monophasic.

6. The film material of any one of claims 1 to 5, which is biphasic.

7. The film material of any one of the preceding claims, where the thickness of the film material is 3 to 90 µm.

8. A process of preparing a film material comprising the step of
contacting a solid phase material and a vapor phase material,
wherein the solid phase material is a metal selected from Group 1 of the Periodic Table, and
wherein the vapor phase material comprises ~~a combination of an amide precursor with an oxide precursor, or~~ a combination of a metal halide precursor and a metalloid halide precursor.

9. The process of claim 8, wherein said Group I metal is selected from the group consisting of lithium, sodium, and potassium.

10. The process of claim 8 or 9, wherein said metal of said metal halide precursor is a transition metal or a Group 14 metal.

11. The process of any one of claims 8 to 10, wherein said metalloid of said metalloid halide precursor is a Group 14 metalloid.

12. The process of any one of claims 8 to 11, wherein the halide of said metal halide precursor or said metalloid halide precursor is selected from the group consisting of fluoride, chloride, bromide and iodide.

~~13. The process of any one of claims 8 to 12, wherein the oxide precursor is water.~~

~~14. The process of any one of claims 8 to 13, wherein the amide precursor is selected from the group consisting of anhydrous ammonia, anhydrous hydrazine, urea and ammonia water.~~

~~15~~13. The process of any one of claims 8 to ~~14~~12, wherein the vapor pressure of the precursor is higher than 22 mmHg at ambient environment conditions (1 atm and 30 °C).

~~16~~14. The process of any one of claims 8 to ~~15~~13, wherein the vapor concentration of the vapor phase material is in the range of 10 to 900 × 10^4 ppm.

~~17~~15. The process of any one of claims 8 to ~~16~~14, wherein the film material is obtained at a growth rate of 0.1 µm/s to 1 µm/s.

~~18~~16. An interphase protected sodium metal anode, wherein said interphase is a film material of any one of claims 1 to 7.

~~19~~17. An electrochemical cell comprising the sodium metal anode of claim ~~18~~16.

~~20~~18. The electrochemical cell of claim ~~19~~17, which is operable at a temperature range of 10 to 40ºC, wherein the sodium anode is in solid form.