



(51) International Patent Classification:

H01M 4/134 (2010.01) *H01M 4/38* (2006.01)
H01M 4/1395 (2010.01) *H01M 10/052* (2010.01)
H01M 4/62 (2006.01)

(21) International Application Number:

PCT/US2017/068181

(22) International Filing Date:

22 December 2017 (22.12.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/438,820 23 December 2016 (23.12.2016) US

(71) Applicants: **SION POWER CORPORATION** [US/US];
2900 E. Elvira Road, Tucson, AZ 85756 (US). **BASF SE** [DE/DE]; Carl-bosch-strasse 38, 67056 Ludwigshafen (DE).

(72) Inventors: **WANG, Zhongchun**; 902 Blair Avenue, Sunnyvale, CA 94087 (US). **DU, Hui**; 1312 N Sahuara Avenue, Tucson, AZ 85712 (US). **SCORDILIS-KELLEY, Chariclea**; 10541 E. Wildfire Dr., Tucson, AZ 85748 (US). **KELLEY, Tracy, Earl**; 10541 E. Wildfire Dr., Tucson, AZ 85748 (US). **SAFONT-SEMPERE, Marina**; Fontanesstrasse 6, 67061 Ludwigshafen (DE). **SCHNEIDER, Holger**; Benckiserplatz, 67059 Ludwigshafen (DE). **WEISS, Thomas**; Pfarrstrasse 28, 68549 Ilvesheim (DE).

(74) Agent: **LEE, Jessamine, N.**; Wolf, Greenfield & Sacks, P.C., 600 Atlantic Avenue, Boston, MA 02210-2206 (US).

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*):

AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

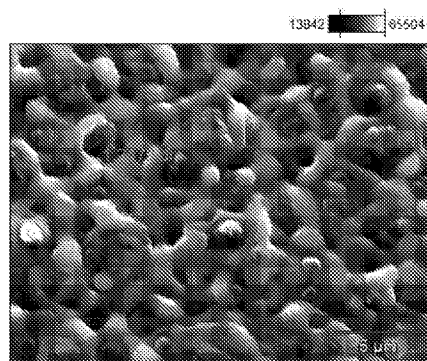
(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*):

ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(54) Title: PROTECTIVE LAYERS COMPRISING METALS FOR ELECTROCHEMICAL CELLS



(57) Abstract: Articles and methods involving protected electrode structures are generally provided. In some embodiments, a protected electrode structure includes an electrode comprising an alkali metal and a protective structure directly adjacent the electrode. In some embodiments, the protective structure comprises elemental carbon and intercalated ions. In some embodiments, the protective structure is a composite protective structure. The composite structure may comprise an alloy comprising an alkali metal, an oxide of an alkali metal, and/or a fluoride salt of an alkali metal.

FIG. 6B



PROTECTIVE LAYERS COMPRISING METALS FOR ELECTROCHEMICAL CELLS**FIELD**

Articles and methods involving protected electrode structures are generally provided.

5

SUMMARY

Articles and methods involving protected electrode structures are generally provided. The subject matter disclosed herein involves, in some cases, interrelated products, alternative solutions to a particular problem, and/or a plurality of different uses of one or more systems and/or articles.

10

In one set of embodiments, protected electrode structures are provided. In some embodiments, a protected electrode structure comprises an electrode and a composite protective structure. The electrode may comprise an alkali metal. The composite protective structure may comprise an alloy comprising the alkali metal and an oxide of the alkali metal.

15

In some embodiments, a protected electrode structure comprises an electrode and a composite protective structure. The electrode may comprise an alkali metal. The composite protective structure may comprise an alloy comprising the alkali metal and a fluoride salt of the alkali metal, wherein the fluoride salt of the alkali metal makes up greater than or equal to 0.1 wt% of the composite protective structure.

20

In some embodiments, a protected electrode structure comprises an electrode and a protective structure. The electrode may comprise an alkali metal. The protective structure may be directly adjacent the electrode, and may comprise elemental carbon and intercalated ions of the alkali metal.

25

Certain embodiments relate to methods for forming protected electrode structures. In some embodiments, a method comprises exposing an electrode comprising an alkali metal to a liquid comprising a plurality of particles, wherein the plurality of particles comprises at least one of a metal-containing species and a metalloid-containing species, and forming a composite protective structure on the electrode, wherein the composite protective structure comprises an alloy comprising the alkali metal.

30

In some embodiments, a method comprises exposing an electrode comprising an alkali metal to a liquid comprising a metal fluoride salt or a metalloid fluoride salt, and forming a

composite protective structure on the electrode, wherein the composite protective structure comprises an alloy comprising the alkali metal and a fluoride salt of the alkali metal.

In some embodiments, a method comprises exposing an electrode comprising an alkali metal to a liquid comprising a plurality of particles, wherein the plurality of particles comprises
5 elemental carbon, and forming a protective structure on the electrode, wherein the protective structure comprises the elemental carbon.

Other advantages and novel features of the present invention will become apparent from the following detailed description of various non-limiting embodiments of the invention when considered in conjunction with the accompanying figures. In cases where the present
10 specification and a document incorporated by reference include conflicting and/or inconsistent disclosure, the present specification shall control. If two or more documents incorporated by reference include conflicting and/or inconsistent disclosure with respect to each other, then the document having the later effective date shall control.

15 BRIEF DESCRIPTION OF THE DRAWINGS

Non-limiting embodiments of the present invention will be described by way of example with reference to the accompanying figures, which are schematic and are not intended to be drawn to scale. In the figures, each identical or nearly identical component illustrated is typically represented by a single numeral. For purposes of clarity, not every component is
20 labeled in every figure, nor is every component of each embodiment of the invention shown where illustration is not necessary to allow those of ordinary skill in the art to understand the invention. In the figures:

FIG. 1 shows a protected electrode structure comprising an electrode and a protective structure (e.g., a protective layer) according to certain embodiments;

25 FIG. 2 shows a method for forming a protected electrode structure according to certain embodiments;

FIG. 3A shows a SEM image of a protective structure that is a protective layer according to certain embodiments;

30 FIG. 3B shows a SEM image of a protective structure that is a protective layer according to certain embodiments;

FIG. 4A shows a SEM image of a protective structure that is a protective layer according to certain embodiments;

FIG. 4B shows a SEM image of a protective structure that is a protective layer according to certain embodiments;

5 FIG. 5A shows a SEM image of a protective structure that is a protective layer according to certain embodiments;

FIG. 5B shows a SEM image of a protective structure that is a protective layer according to certain embodiments;

10 FIG. 6A shows a SEM image of a protective structure that is a protective layer according to certain embodiments;

FIG. 6B shows a SEM image of a protective structure that is a protective layer according to certain embodiments;

FIG. 6C shows a SEM image of a protective structure that is a protective layer according to certain embodiments;

15 FIG. 7A shows a SEM image of a protective structure that is a protective layer according to certain embodiments;

FIG. 7B shows a SEM image of a protective structure that is a protective layer according to certain embodiments;

20 FIG. 8A shows a SEM image of a protective structure that is a protective layer according to certain embodiments; and

FIG. 8B shows a SEM image of a protective structure that is a protective layer according to certain embodiments.

DETAILED DESCRIPTION

25 Articles and methods involving protected electrode structures are generally provided. For instance, a protected electrode structure may comprise an electrode and a protective structure directly adjacent to the electrode. The protective structure may serve to protect the electrode from undesirable reactions with one or more species in the electrochemical cell (e.g., an electrolyte), and/or to prevent or substantially reduce the exposure of the electrode to an
30 electrolyte. In some embodiments, the protective structure may be capable of transporting ions which participate in electrochemical reactions (e.g., from a side of the protective structure

proximate an electrolyte to an opposite side of the protective structure proximate the electrode) and/or may be ionically conductive. The protective structure may also have one or more other properties that result in improved cell performance. For instance, the protective structure may be connected to the electrode by bonding sufficiently strong to prevent its delamination during
5 typical handling and electrochemical cell cycling. As another example, the protective structure may have good flexibility and may be capable of accommodating typical changes in size of the electrode during electrochemical cell cycling (e.g., electrode expansion during discharging, electrode contraction during charging) while still maintaining its protective functionality (e.g., by not undergoing fracture). In some embodiments, the protective structure may form a stable solid
10 electrolyte interface when positioned in an electrochemical cell. Compositions of protective structures with particular utility and advantageous methods for forming protective structures are described in more detail below.

FIG. 1 depicts a protected electrode structure 100 according to some embodiments of the invention. As shown illustratively in this figure, protected electrode structure 100 comprises
15 electrode 110 and protective structure 120 adjacent to electrode 110. The protective structure may protect the electrode by, for example, preventing exposure of the electrode to an electrolyte. In some embodiments, the protective structure may be substantially impermeable to an electrolyte.

In some embodiments, the protective structure is directly adjacent to the electrode. An
20 electrochemical cell component (e.g., an electrode, a protected electrode structure) referred to as being “disposed on,” “disposed between,” “on,” or “adjacent” another electrochemical cell component (s) means that it can be directly disposed on, disposed between, on, or adjacent the electrochemical cell component (s), or an intervening electrochemical cell component may also be present. For example, an additive electrochemical cell component (e.g., a protective
25 structure) described herein that is adjacent an electrode may be directly adjacent (e.g., may be in direct physical contact with) the electrode, or an intervening electrochemical cell component (e.g., a passivation layer) may be positioned between the electrode and the additive layer. An electrochemical cell component that is “directly adjacent,” “directly on,” or “in contact with,”
30 another electrochemical cell component means that no intervening electrochemical cell component is present. It should also be understood that when an electrochemical cell component is referred to as being “disposed on,” “disposed between,” “on,” or “adjacent” another

electrochemical cell component (s), it may be covered by, on or adjacent the entire electrochemical cell component (s) or a part of the electrochemical cell component (s).

The protective electrode may be formed such that protective structure 120 is integrally connected with electrode 110 (e.g., the electroactive portion). For example, the structure may be formed such that there is no clear distinction between when the protective structure starts and ends and where the electrode starts and ends (e.g., no distinct, separate electroactive and protective layers). In some cases, integrally connected components have a cohesive/adhesive strength between two materials that is at least as great as the yield strength of each of the materials (e.g., the electroactive material and the material used to form the protected electrode).

Although depicted as a homogeneous structure in FIG. 1, a protective structure should be understood to possibly comprise more than one constituent materials in some embodiments (i.e., the protective structure can be a composite protective structure). For example, the protective structure may comprise at least two constituent materials, at least three constituent materials, or more constituent materials. As used herein, a constituent material should be understood to refer to any species that includes only a single phase (e.g., a metal, an alloy, a ceramic, a polymer, or a solution). That is, a single constituent material should not be understood to encompass mixtures, composites, and the like. Materials such as mixtures and composites should be understood to comprise at least two constituent materials. In some embodiments, two or more constituent materials such as an alloy (e.g., a first constituent material) and a ceramic (e.g., a second constituent material) may form a cross-linked structure.

If the protective structure comprises at least two constituent materials, they may be disposed with respect to each other in any suitable manner. For instance, a protective structure may comprise at least two constituent materials and the first constituent material may surround the second constituent material (e.g., in a core shell structure), the first substance may form a matrix in which the second constituent material is disposed, and/or both the first constituent material and the second constituent material may form interpenetrating networks that span the protective structure (or at least 50 vol% of the protective structure, at least 75 vol% of the protective structure, at least 90 vol% of the protective structure, at least 95% of the protective structure, or at least 99 vol% of the protective structure). That is, the first and second constituent materials may both form networks that are topologically connected, and each network may be enclosed by a volume that spans at least 50% of the protective structure, at least 75% of the

protective structure, at least 90% of the protective structure, at least 95% of the protective structure, at least 99% of the protective structure, or the entirety of the protective structure.

In some embodiments, as will be described in further detail below, a protective structure may comprise pores and/or particles. In such cases, the arrangement of two or more constituent materials with respect to each other should be understood to refer to any or all of the arrangement of the constituent materials within individual particles, the arrangement of the constituent materials within a matrix surrounding the pores, and the arrangement of the constituent materials within the protective structure as a whole.

In some embodiments, a protective structure may comprise exactly one constituent material.

In some embodiments, each constituent material of a protective structure may be a material that is not a precursor material. That is, the protective structure may be formed from one or more precursor materials (e.g., halide salts such as fluoride salts; particles such as particles that comprise a metal oxide, a metalloid oxide, and/or a metal) and none of the precursor materials may be present in the protective structure. However, in other embodiments, the protective structure may comprise one or more precursor materials (e.g., the protective structure may comprise a halide salt such as a non-alkali (e.g., non-lithium) fluoride salt, a metal or metalloid oxide, or a metal or metalloid). In some embodiments, the protective structure may comprise metal-containing species, such as a metal oxide or a metal in a metallic phase. In some embodiments, the protective structure may comprise metalloid-containing species, such as a metalloid oxide or a metalloid in a metalloid phase.

In some embodiments, a protective structure (e.g., a protective structure formed by a method described herein, a composite protective structure) may comprise at least one alloy (a metal alloy). Typically, an alloy included in the protective structure comprises at least two species. The first species includes a metal that is also included in the electrode (e.g., an alkali metal such as lithium). The alloy also includes a second species. In some embodiments, the second species is not included in the electrode, or is included in the electrode in small amounts (e.g., less than or equal to 10 wt%, less than or equal to 8 wt%, less than or equal to 6 wt%, less than or equal to 4 wt%, less than or equal to 2 wt%, or less than or equal to 1 wt% with respect to the weight of the electrode). Other optional components may also be present in the alloy. In some embodiments, the second species may be a metal (e.g., an alkaline earth metal, a transition

metal, a post transition metal) or a metalloid. Non-limiting examples of suitable metals and metalloids include Sn, Zn, In, Al, Mg, Ga, Ag, Cd, Pb, Bi, Sb, Si, Ge, and As. In some embodiments, the second species is a non-alkali metal. In some embodiments, the protective structure may include one or more of the following alloys: Li₃Sb, Li₄Sn, LiZn, and LiZn₁₃, LiAl₃,
5 Li₃In, LiMg, LiGa, LiAg, Li₂Cd, Li₂Pb, Li₃Bi, Li₄Si, Li₄Ge, Li₃As.

In some embodiments, a protective structure (e.g., a protective structure formed by a method described herein, a composite protective structure) may comprise at least one alloy and the alloy may make up greater than or equal to 30 wt% of the protective structure, greater than or equal to 40 wt% of the protective structure, greater than or equal to 50 wt% of the protective
10 structure, greater than or equal to 60 wt% of the protective structure, greater than or equal to 70 wt% of the protective structure, greater than or equal to 80 wt% of the protective structure, greater than or equal to 90 wt% of the protective structure, greater than or equal to 95 wt% of the protective structure, greater than or equal to 97.5 wt% of the protective structure, greater than or equal to 99 wt% of the protective structure, greater than or equal to or 99.5 wt% of the protective
15 structure. In some embodiments, a protective structure may comprise at least one alloy and the alloy may make up less than or equal to 99.9 wt% of the protective structure, less than or equal to 99.5 wt% of the protective structure, less than or equal to 99 wt% of the protective structure, less than or equal to 97.5 wt% of the protective structure, less than or equal to 95 wt% of the protective structure, less than or equal to 90 wt% of the protective structure, less than or equal to
20 80 wt% of the protective structure, less than or equal to 70 wt% of the protective structure, less than or equal to 60 wt% of the protective structure, less than or equal to 50 wt% of the protective structure, or less than or equal to 40 wt% of the protective structure. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 30 wt% and less than or equal to 99.9 wt%, or greater than or equal to 50 wt% and less than or equal to 90 wt%). Other ranges
25 are also possible.

In some embodiments, a protective structure (e.g., a protective structure formed by a method described herein, a composite protective structure) includes an alloy that comprises an alkali metal (e.g., the same alkali metal that is included in the electrode), which may be a first species of the alloy, and the alkali metal (e.g., first species) makes up greater than or equal to
30 0.001 wt% of the alloy, greater than or equal to 0.002 wt% of the alloy, greater than or equal to 0.005 wt% of the alloy, greater than or equal to 0.01 wt% of the alloy, greater than or equal to

0.02 wt% of the alloy, greater than or equal to 0.05 wt% of the alloy, greater than or equal to 0.1 wt% of the alloy, greater than or equal to 0.2 wt% of the alloy, greater than or equal to 0.5 wt% of the alloy, greater than or equal to 1 wt% of the alloy, greater than or equal to 2 wt% of the alloy, greater than or equal to 5 wt% of the alloy, greater than or equal to 10 wt% of the alloy, or
5 greater than or equal to 20 wt% of the alloy. In some embodiments, the alkali metal (e.g., first species) makes up less than or equal to 50 wt% of the alloy, less than or equal to 20 wt% of the alloy, less than or equal to 10 wt% of the alloy, less than or equal to 5 wt% of the alloy, less than or equal to 2 wt% of the alloy, less than or equal to 1 wt% of the alloy, less than or equal to 0.5 wt% of the alloy, less than or equal to 0.2 wt% of the alloy, less than or equal to 0.1 wt% of the
10 alloy, less than or equal to 0.05 wt% of the alloy, less than or equal to 0.02 wt% of the alloy, less than or equal to 0.01 wt% of the alloy, less than or equal to 0.005 wt% of the alloy, or less than or equal to 0.002 wt% of the alloy. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 0.001 wt% of the alloy and less than or equal to 50 wt% of the alloy). Other ranges are also possible.

15 In some embodiments, a protective structure (e.g., a protective structure formed by a method described herein, a composite protective structure) includes an alloy comprising a second species (e.g., a non-alkali metal), and the second species makes up greater than or equal to 50 wt% of the alloy, greater than or equal to 75 wt% of the alloy, greater than or equal to 90 wt% of the alloy, greater than or equal to 95 wt% of the alloy, greater than or equal to 99 wt% of the
20 alloy, greater than or equal to 99.5 wt% of the alloy, greater than or equal to 99.9 wt% of the alloy, greater than or equal to 99.95 wt% of the alloy, or greater than or equal to 99.99 wt% of the alloy. In some embodiments, the second species (e.g., non-alkali metal) makes up less than or equal to 99.995 wt% of the alloy, less than or equal to 99.99 wt% of the alloy, less than or equal to 99.95 wt% of the alloy, less than or equal to 99.9 wt% of the alloy, less than or equal to
25 99.5 wt% of the alloy, less than or equal to 99 wt% of the alloy, less than or equal to 95 wt% of the alloy, less than or equal to 90 wt% of the alloy, or less than or equal to 75 wt% of the alloy. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 50 wt% of the alloy and less than or equal to 99.995 wt% of the alloy). Other ranges are also possible.

30 In some embodiments, a protective structure (e.g., a protective structure formed by a method described herein, a composite protective structure) may comprise at least one oxide. In

some embodiments, the protective structure may comprise two or more oxides. In some
embodiments, one or more of the oxide(s) may be insoluble or sparingly soluble (e.g., less than 2
wt% soluble, less than 1 wt% soluble, less than 0.5 wt% soluble) in one or more fluids to which
it is exposed (e.g., a fluid comprising a precursor for the protective structure, an electrolyte in an
5 electrochemical cell comprising the protected electrode structure). The protective structure may
comprise an oxide of a metal included in the electrode (e.g., an oxide of an alkali metal such as
lithium). In some embodiments, the protective structure may comprise an oxide that exclusively
comprises oxygen and a metal included in the electrode. For example, the protective structure
may comprise Li_2O . In some embodiments, the protective structure may comprise an oxide that
10 does not include a metal included in the electrode or is included in the electrode in small amounts
(e.g., less than or equal to 10 wt%, less than or equal to 8 wt%, less than or equal to 6 wt%, less
than or equal to 4 wt%, less than or equal to 2 wt%, or less than or equal to 1 wt% with respect to
the weight of the electrode). Such oxides may comprise one or more of Sn, Zn, In, Al, Mg, Ga,
Ag, Cd, Pb, Bi, Sb, Si, Ge, and As (e.g., ZnO , In_2O_3). In some embodiments, a protective
15 structure may comprise both an alloy as described above and an oxide, and a metal or metalloid
may be present in both the alloy and the oxide (e.g., the protective structure may comprise both
 LiZn and ZnO , where Zn is present in both the LiZn alloy and the ZnO oxide). In some
embodiments, the oxide comprising the metal or metalloid may be a precursor that has not fully
reacted with the electrode.

20 In some embodiments, a protective structure may comprise at least one oxide (e.g., Li_2O ,
 ZnO), and the oxide may make up greater than or equal to 0.1 wt% of the protective structure,
greater than or equal to 0.2 wt% of the protective structure, greater than or equal to 0.5 wt% of
the protective structure, greater than or equal to 1 wt% of the protective structure, greater than or
equal to 2 wt% of the protective structure, greater than or equal to 5 wt% of the protective
25 structure, greater than or equal to 10 wt% of the protective structure, greater than or equal to 20
wt% of the protective structure, greater than or equal to 30 wt% of the protective structure,
greater than or equal to 40 wt% of the protective structure, greater than or equal to 50 wt% of the
protective structure, or greater than or equal to 60 wt% of the protective structure,. In some
embodiments, a protective structure comprises at least one oxide, and the oxide makes up less
30 than or equal to 70 wt% of the protective structure, less than or equal to 60 wt% of the protective
structure, less than or equal to 50 wt% of the protective structure, less than or equal to 40 wt% of

the protective structure, less than or equal to 30 wt% of the protective structure, less than or equal to 20 wt% of the protective structure, less than or equal to 10 wt% of the protective structure, less than or equal to 5 wt% of the protective structure, less than or equal to 2 wt% of the protective structure, less than or equal to 1 wt% of the protective structure, less than or equal to 0.5 wt% of the protective structure, or less than or equal to 0.2 wt% of the protective structure. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 0.1 wt% of the protective structure and less than or equal to 70 wt% of the protective structure, or greater than or equal to 10 wt% of the protective structure and less than or equal to 50 wt% of the protective structure). Other ranges are also possible.

10 In some embodiments, a protective structure (e.g., a protective structure formed by a method described herein, a composite protective structure) may comprise a halide salt, such as a fluoride salt. Other examples of halide salts include chloride salts, bromide salts, and iodide salts. The halide salt may comprise a metal included in the electrode (e.g., it may be a fluoride salt (e.g., LiF) of an alkali metal such as lithium). In some embodiments, the halide (e.g.,
15 fluoride) salt may be insoluble or sparingly soluble (e.g., less than 2 wt% soluble, less than 1 wt% soluble, less than 0.5 wt% soluble) in one or more fluids to which it is exposed (e.g., a fluid comprising a precursor for the protective structure, an electrolyte in an electrochemical cell comprising the protected electrode structure). When present, the halide salt (e.g., a fluoride salt) may make up any suitable amount of the protective structure. In some embodiments, the halide
20 salt (e.g., a fluoride salt) makes up greater than or equal to 0.1 wt% of the protective structure, greater than or equal to 0.2 wt% of the protective structure, greater than or equal to 0.5 wt% of the protective structure, greater than or equal to 1 wt% of the protective structure, greater than or equal to 2 wt% of the protective structure, greater than or equal to 5 wt% of the protective structure, greater than or equal to 10 wt% of the protective structure, greater than or equal to 20
25 wt% of the protective structure, greater than or equal to 30 wt% of the protective structure, greater than or equal to 40 wt% of the protective structure, greater than or equal to 50 wt% of the protective structure, or greater than or equal to 60 wt% of the protective structure. In some embodiments, the fluoride salt makes up less than or equal to 70 wt% of the protective structure, less than or equal to 60 wt% of the protective structure, less than or equal to 50 wt% of the
30 protective structure, less than or equal to 40 wt% of the protective structure, less than or equal to 30 wt% of the protective structure, less than or equal to 20 wt% of the protective structure, less

than or equal to 10 wt% of the protective structure, less than or equal to 5 wt% of the protective structure, less than or equal to 2 wt% of the protective structure, less than or equal to 1 wt% of the protective structure, less than or equal to 0.5 wt% of the protective structure, or less than or equal to 0.2 wt% of the protective structure. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 0.1 wt% of the protective structure and less than or equal to 70 wt% of the protective structure, or greater than or equal to 10 wt% of the protective structure and less than or equal to 50 wt% of the protective structure). Other ranges are also possible.

In some embodiments, a protective structure (e.g., a protective structure formed by a method described herein) may comprise elemental carbon. The elemental carbon may be in any suitable form, non-limiting examples of which include graphite, carbon nanotubes, carbon nanofibers, graphene, and graphene oxide. In some embodiments, the elemental carbon further comprises intercalated ions, such as intercalated ions of a metal included in the electrode (e.g., an alkali metal such as lithium). For example, the protective structure may comprise a lithium-carbon intercalation compound. Two examples of such materials are graphite comprising intercalated lithium (i.e., Li_xC_6) and lithium carbide. In some embodiments, the elemental carbon and any intercalated ions may make up a relatively large amount of the protective structure. For instance, the elemental carbon and any intercalated ions may make up greater than or equal to 75 wt%, greater than or equal to 90 wt%, greater than or equal to 95 wt%, greater than or equal to 99 wt%, or greater than or equal to 99.5 wt% of the protective structure. The elemental carbon and any intercalated ions may make up less than or equal to 100 wt% of the protective structure, less than or equal to 99.5 wt% of the protective structure, less than or equal to 99 wt% of the protective structure, less than or equal to 95 wt% of the protective structure, less than or equal to 90 wt% of the protective structure, or less than or equal to 75 wt% of the protective structure. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 75 wt% of the protective structure and less than or equal to 100 wt% of the protective structure). Other ranges are also possible.

In some embodiments, a protective structure (e.g., a protective structure formed by a method described herein, a composite protective structure) may comprise a metal (e.g., a second metal) that is not alloyed with a metal (e.g., a first metal) that is included in the electrode (e.g., the second metal is not alloyed with an alkali metal such as lithium). Additionally or

alternatively, a protective structure (e.g., a protective structure formed by a method described herein, a composite protective structure) may comprise a metal (e.g., a second metal) that does not form an alloy with a metal (e.g., a first metal) that is included in the electrode (e.g., the second metal does not form an alloy with an alkali metal such as lithium). In some
5 embodiments, a protective structure (e.g., a protective structure formed by a method described herein, a composite protective structure) may comprise a metalloid that is not alloyed with a metal that is included in the electrode (e.g., the metalloid is not alloyed with an alkali metal such as lithium). Additionally or alternatively, a protective structure (e.g., a protective structure formed by a method described herein, a composite protective structure) may comprise a
10 metalloid that does not form an alloy with a metal that is included in the electrode (e.g., the metalloid does not form an alloy with an alkali metal such as lithium). For instance, the metal (e.g., second metal) may be one or more of Cu, Ni, and Fe. The metal (e.g., second metal) may be in a metallic phase, in some embodiments. The metalloid may be in a metalloid phase, in some embodiments. In some embodiments, a metal (e.g., a second metal) or metalloid that is not
15 alloyed with a metal that is included in the electrode may, advantageously, assist electronic conduction and/or function as a current collector.

As used herein, a metal (e.g., a second metal) does not form an alloy with another metal (e.g., a first metal) if, after being placed in direct contact with the metal (e.g., first metal) for a period of one hour at a temperature of 130 °C, it does not form an alloy with the metal (e.g., first
20 metal) observable by X-ray diffraction. As used herein, a metalloid does not form an alloy with a metal if, after being placed in direct contact with the metal for a period of one hour at a temperature of 130 °C, it does not form an alloy with the metal observable by X-ray diffraction.

The metal (e.g., second metal) and/or the metalloid may be present in the protective structure in any suitable amount. In some embodiments, the metal or metalloid may make up
25 greater than or equal to 1 wt% of the protective structure, greater than or equal to 2 wt% of the protective structure, greater than or equal to 5 wt% of the protective structure, greater than or equal to 10 wt% of the protective structure, greater than or equal to 20 wt% of the protective structure, greater than or equal to 50 wt% of the protective structure, greater than or equal to 70 wt% of the protective structure, greater than or equal to 90 wt% of the protective structure,
30 greater than or equal to 95 wt% of the protective structure, greater than or equal to 97.5 wt% of the protective structure, or greater than or equal to 99 wt% of the protective structure. In some

embodiments, the metal or metalloid may make up less than or equal to 100 wt% of the protective structure, less than or equal to 99 wt% of the protective structure, less than or equal to 97.5 wt% of the protective structure, less than or equal to 95 wt% of the protective structure, less than or equal to 90 wt% of the protective structure, less than or equal to 70 wt% of the protective structure, less than or equal to 50 wt% of the protective structure, less than or equal to 20 wt% of the protective structure, less than or equal to 10 wt% of the protective structure, less than or equal to 5 wt% of the protective structure, or less than or equal to 2 wt% of the protective structure. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 1 wt% and less than or equal to 100 wt% of the protective structure). Other ranges are also possible. A protective structure (e.g., a protective structure formed by a method described herein, a composite protective structure) may have any suitable thickness. In some embodiments, the protective structure has a thickness of greater than or equal to 20 nm, greater than or equal to 50 nm, greater than or equal to 100 nm, greater than or equal to 500 nm, greater than or equal to 1 micron, or greater than or equal to 2 microns. In some embodiments, the protective structure has a thickness of less than or equal to 5 microns, less than or equal to 4 microns, less than or equal to 3 microns, less than or equal to 2 microns, less than or equal to 1 micron, less than or equal to 500 nm, less than or equal to 200 nm, less than or equal to 100 nm, or less than or equal to 50 nm. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 20 nm and less than or equal to 5 microns). Other ranges are also possible.

In some embodiments, a protective structure (e.g., a protective structure formed by a method described herein, a composite protective structure) may comprise pores. In some cases, at least 50% of the pore volume, at least 75% of the pore volume, or at least 90% of the pore volume is made up of pores with a cross-sectional diameter of greater than or equal to 0.001 microns, greater than or equal to 0.002 microns, greater than or equal to 0.005 microns, greater than or equal to 0.01 microns, greater than or equal to 0.02 microns, greater than or equal to 0.05 microns, greater than or equal to 0.1 microns, or greater than or equal to 0.2 microns. In some cases, at least 50% of the pore volume, at least 75% of the pore volume, or at least 90% of the pore volume is made up of pores with a cross-sectional diameter of less than or equal to 0.5 microns, less than or equal to 0.2 microns, less than or equal to 0.1 microns, less than or equal to 0.05 microns, less than or equal to 0.02 microns, less than or equal to 0.01 microns, less than or

equal to 0.005 microns, or less than or equal to 0.002 microns. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 0.001 microns and less than or equal to 0.5 microns). Other ranges are also possible.

As used herein, the “cross-sectional diameter” of a pore refers to a cross-sectional
5 diameter as measured using ASTM Standard Test D4284-07. One of ordinary skill in the art would be capable of calculating the distribution of cross-sectional diameters and the average cross-sectional diameter of the pores within a layer using mercury intrusion porosimetry as described in ASTM standard D4284-07, which is incorporated herein by reference in its entirety. For example, the methods described in ASTM standard D4284-92 can be used to produce a
10 distribution of pore sizes plotted as the cumulative intruded pore volume as a function of pore diameter. To calculate the fraction of the total pore volume within the sample that is occupied by pores within a given range of pore diameters, one would: (1) calculate the area under the curve that spans the given range over the x-axis, and (2) divide the area calculated in step (1) by the total area under the curve. Optionally, in cases where the article includes pore sizes that lie
15 outside the range of pore sizes that can be accurately measured using ASTM standard D4284-92, porosimetry measurements may be supplemented using BET surface analysis, as described, for example, in S. Brunauer, P. H. Emmett, and E. Teller, *J. Am. Chem. Soc.*, 1938, 60, 309, which is incorporated herein by reference in its entirety.

In some aspects, a protective structure (e.g., a protective structure formed by a method
20 described herein, a composite protective structure) may be porous. That is, at least an appreciable fraction of the volume of the protective structure may be made up of pores. In some embodiments, pores make up greater than or equal to 2 vol%, greater than or equal to 5 vol%, greater than or equal to 10 vol%, greater than or equal to 20 vol%, greater than or equal to 30 vol%, greater than or equal to 40 vol%, greater than or equal to 50 vol%, greater than or equal to
25 60 vol%, greater than or equal to 70 vol%, or greater than or equal to 80 vol% of the protective structure may be made up of pores. In some embodiments, pores make up less than or equal to 90 vol% of the protective structure, less than or equal to 80 vol% of the protective structure, less than or equal to 70 vol% of the protective structure, less than or equal to 60 vol% of the protective structure, less than or equal to 50 vol% of the protective structure less than or equal to
30 40 vol% of the protective structure, less than or equal to 30 vol% of the protective structure, or less than or equal to 20 vol% of the protective structure. Combinations of the above-referenced

ranges are also possible (e.g., greater than or equal to 10 vol% and less than or equal to 90 vol%). Other ranges are also possible. Porosity can be determined, for example, by mercury porosimetry.

5 In some embodiments, a protective structure (e.g., a protective structure formed by a method described herein, a composite protective structure) may comprise particles. The particles may comprise one or more constituent materials of the protective structure (e.g., one or more of an alloy, an oxide, a fluoride salt, elemental carbon, a metal, and a metalloid).

10 When a protective structure (e.g., a protective structure formed by a method described herein, a composite protective structure) includes particles, the particles may have any suitable average cross-sectional diameter. As used herein, the cross-sectional diameter of a particle refers to the diameter of a sphere that encloses a volume that is equivalent to the volume of the particle. The average cross-sectional diameter of a plurality of particles refers to the number average cross-sectional diameter of the particles forming the plurality. The average cross-sectional diameter may be determined by SEM. In some embodiments, the particles have an average
15 cross-sectional diameter of greater than or equal to 20 nm, greater than or equal to 50 nm, greater than or equal to 100 nm, greater than or equal to 500 nm, greater than or equal to 1 micron, or greater than or equal to 2 microns. In some embodiments, the particles have an average cross-sectional diameter of less than or equal to 5 microns, less than or equal to 4 microns, less than or equal to 3 microns, less than or equal to 2 microns, less than or equal to 1 micron, less than or equal to 500 nm, less than or equal to 200 nm, less than or equal to 100 nm, or less than or equal
20 to 50 nm. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 20 nm and less than or equal to 5 microns). Other ranges are also possible. In some embodiments, the particles (e.g., metal particles, metalloid particles, metal oxide particles, metalloid oxide particles) may comprise nanoparticles, which are particles with an average cross-sectional diameter of less than or equal to 1 micron.
25

In some embodiments, particles may make up a relatively large amount of a protective structure (e.g., a protective structure formed by a method described herein, a composite protective structure). For example, particles may make up greater than or equal to 50 wt% of the protective structure, greater than or equal to 60 wt% of the protective structure, greater than or
30 equal to 70 wt% of the protective structure, greater than or equal to 80 wt% of the protective structure, greater than or equal to 90 wt% of the protective structure, greater than or equal to 95

wt% of the protective structure, greater than or equal to 97.5 wt% of the protective structure, greater than or equal to 99 wt% of the protective structure, or greater than or equal to 99.5 wt% of the protective structure. In some embodiments, particles may make up less than or equal to 100 wt% of the protective structure, less than or equal to 99.5 wt% of the protective structure, 5 less than or equal to 99 wt% of the protective structure, less than or equal to 97.5 wt% of the protective structure, less than or equal to 95 wt% of the protective structure, less than or equal to 90 wt% of the protective structure, less than or equal to 80 wt% of the protective structure less than or equal to 70 wt% of the protective structure or less than or equal to 60 wt% of the protective structure. Combinations of the above-referenced ranges are also possible (e.g., greater 10 than or equal to 50 wt% of the protective structure and less than or equal to 100 wt% of the protective structure). Other ranges are also possible.

In some embodiments, one or more (or substantially all) of the particles in the protective structure may have a core-shell structure. That is, the particles may have a structure where a constituent material or combination of constituent materials is mostly present within a central 15 region of the particle and a different constituent material or combination of constituent materials is present in a region of the particle that surrounds the central region (e.g., forming a shell). In some embodiments, an alloy (e.g., an alloy of a metal included in the electrode, an alloy comprising an alkali metal such as lithium) may form the shell of the core-shell structure. In some embodiments, an oxide (e.g., an oxide of a metal included in the electrode, an oxide of an 20 alkali metal such as lithium, an oxide of a metal included in an alloy) may form the core of the core-shell structure.

In some embodiments, a protective structure (e.g., a protective structure formed by a method described herein, a composite protective structure) may have a relatively high ionic conductivity. In certain embodiments, the protective structure may have an ionic conductivity of 25 greater than or equal to 10^{-7} S/cm, greater than or equal to 10^{-6} S/cm, greater than or equal to 10^{-5} S/cm, greater than or equal to 10^{-4} S/cm, greater than or equal to 10^{-3} S/cm, greater than or equal to 10^{-2} S/cm, greater than or equal to 10^{-1} S/cm, greater than or equal to 1 S/cm, or greater than or equal to 10 S/cm. In certain embodiments, the protective structure may have an ionic conductivity of less than or equal to 100 S/cm, less than or equal to 10 S/cm, less than or equal to 30 1 S/cm, less than or equal to 10^{-1} S/cm, less than or equal to 10^{-2} S/cm, less than or equal to 10^{-3} S/cm, less than or equal to 10^{-4} S/cm, less than or equal to 10^{-5} S/cm, or less than or equal to 10^{-6}

S/cm. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 10^{-4} S/cm and less than or equal to 100 S/cm). Other ranges are also possible. The ionic conductivity of the protective structure may be determined using EIS.

As described above, certain inventive methods relate to the formation of a protective structure (e.g., a composite protective structure) on an electrode. FIG. 2 shows one such method in accordance with certain embodiments. As depicted illustratively therein, a method may comprise exposing an electrode 210 to a fluid 230 (e.g., a liquid) and forming protective structure 220 on (e.g., directly adjacent to) electrode 210. While FIG. 2 shows exposure of the electrode to the fluid by immersing (e.g., dipping) the electrode in the fluid, other methods of exposing the electrode to the fluid are also possible. For example, the fluid may be sprayed or dripped onto the electrode. In some embodiments, the fluid may be coated onto the electrode. For instance, one or more of doctor-blade coating, slot-die coating, roll coating, and brush coating may be employed. In some embodiments, the fluid may be a liquid.

In some embodiments, an electrode is exposed to a fluid that comprises a plurality of particles. In some embodiments, the electrode is exposed to a fluid that comprises more than one plurality of particles. The particles may be particle precursors that transform into the protective structure and/or one or more components thereof. The particles may be suspended and/or dispersed within the fluid and may form a colloidal suspension in some embodiments. In some embodiments, the particles comprise a metal-containing species (e.g., a metal, a second metal as described herein) and/or a metalloid containing species. The metal-containing species or metalloid-containing species may be an oxide, such as a metal oxide or metalloid oxide. In some embodiments, the metal or metalloid may be one or more of Sn, Zn, In, Al, Mg, Ga, Ag, Cd, Pb, Bi, Sb, Si, Ge, and As (e.g., the metal-containing species may be ZnO, the metal-containing species may be alumina). In some embodiments, the metal-containing species (e.g., a metal, a second metal as described herein) or metalloid-containing species may comprise one or more metals in a metallic phase and/or metalloids in a metalloid phase. In some embodiments, the metal or metalloid may be one or more of Sn, Zn, In, Al, Mg, Ga, Ag, Cd, Pb, Bi, Sb, Si, Ge, As, Cu, Ni, and Fe. In some embodiments, some or all of the particles (e.g., the metal oxide or metalloid oxide particles, if present; the metallic metal and/or metalloid phase metalloid particles, if present) may be in the form of a powder. In some embodiments, the particles comprise elemental carbon, such as graphite, carbon nanotubes, carbon nanofibers, graphene,

and/or graphene oxide. In some cases, the powder may be a fumed powder (e.g., a fumed alumina powder). In some embodiments, the powder may be a nanopowder (e.g., an aluminum nanopowder).

The particles, if present, may have any suitable average cross-sectional diameter. In
5 some embodiments, the particles have an average cross-sectional diameter of greater than or
equal to 20 nm, greater than or equal to 50 nm, greater than or equal to 100 nm, greater than or
equal to 500 nm, greater than or equal to 1 micron, or greater than or equal to 2 microns. In
some embodiments, the particles have an average cross-sectional diameter of less than or equal
10 500 nm, less than or equal to 200 nm, less than or equal to 100 nm, or less than or equal to 50
nm. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to
20 nm and less than or equal to 5 microns). Other ranges are also possible. In some
embodiments, the particles (e.g., metal particles, metalloid particles, metal oxide particles,
metalloid oxide particles) may comprise nanoparticles, which are particles with an average cross-
15 sectional diameter of less than or equal to 1 micron. The average cross-sectional diameter may
be determined by SEM.

When present, the particles (e.g., particles that comprise a metal-containing species or a
metalloid-containing species, particles that comprise elemental carbon) may make up any
suitable amount of the fluid to which the electrode is exposed. For instance, the particles may
20 make up greater than or equal to 0.5 wt%, greater than or equal to 1 wt%, greater than or equal to
2 wt%, greater than or equal to 5 wt%, greater than or equal to 10 wt%, or greater than or equal
to 20 wt% of the fluid to which the electrode is exposed. The particles may make up less than or
equal to 30 wt%, less than or equal to 20 wt%, less than or equal to 10 wt%, less than or equal to
5 wt%, less than or equal to 2 wt%, or less than or equal to 1 wt% of the fluid to which the
25 electrode is exposed. Combinations of the above-referenced ranges are also possible (e.g.,
greater than or equal to 0.5 wt% and less than or equal to 30 wt%). Other ranges are also
possible.

In some embodiments, the electrode is exposed to a fluid that comprises a fluoride salt,
such as a metal fluoride salt or a metalloid fluoride salt. For example, the fluoride salt may
30 comprise one or more of Sn, Zn, In, Al, Mg, Ga, Ag, Cd, Pb, Bi, Sb, Si, Ge, and As (e.g., SbF₃,
SnF₂). In some embodiments, the fluoride salt may be dissolved in the fluid. In some

embodiments, a cation of the fluoride salt may form a complex with a component (e.g., a solvent) present in the fluid (e.g., the fluid may include pyridine and Sn(II) ions, and Sn(II) ions may form a complex with pyridine).

When present, the fluoride salt (e.g., metal fluoride salt, metalloid fluoride salt) may
5 make up any suitable amount of the fluid to which the electrode is exposed. For instance, the particles may make up greater than or equal to 0.5 wt%, greater than or equal to 1 wt%, greater than or equal to 2 wt%, greater than or equal to 5 wt%, greater than or equal to 10 wt%, or greater than or equal to 20 wt% of the fluid to which the electrode is exposed. The fluoride salt may make up less than or equal to 30 wt%, less than or equal to 20 wt%, less than or equal to 10
10 wt%, less than or equal to 5 wt%, less than or equal to 2 wt%, or less than or equal to 1 wt% of the fluid to which the electrode is exposed. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 0.5 wt% and less than or equal to 30 wt%). Other ranges are also possible.

In some embodiments, the electrode is exposed to a fluid that comprises a first plurality
15 of particles comprising a metal in a metallic phase and comprises a second plurality of particles comprising a metal in a non-metallic phase. The metal in the non-metallic phase may be a component of a halide salt (e.g., a fluoride salt) and/or a component of an oxide. The first plurality of particles may comprise a metal (e.g., a second metal) that does not form an alloy with a metal (e.g., a first metal) that is included in the electrode (e.g., the second metal does not form
20 an alloy with an alkali metal such as lithium). Additionally or alternatively, the first plurality of particles may comprise a metal (e.g., a third metal) that forms an alloy with a metal (e.g., a first metal) that is included in the electrode (e.g., the third metal forms an alloy with an alkali metal such as lithium). The first plurality of particles may comprise a metal in a metallic phase that is
25 the same type of metal as metal in a non-metallic phase included in the second plurality of particles (e.g., the first plurality of particles may comprise zinc and the second plurality of particles may comprise zinc oxide; the first plurality of particles may comprise zinc and the second plurality of particles may comprise zinc fluoride). Additionally or alternatively, the first plurality of particles may comprise a metal that is a different type of metal than a type of metal in
30 a non-metallic phase included in the second plurality of particles (e.g., the first plurality of particles may comprise copper, and the second plurality of particles may comprise zinc oxide; the first plurality of particles may comprise copper, and the second plurality of particles may

comprise zinc fluoride). In some embodiments, the first plurality of particles may comprise a metal in a metallic phase that is the same type of metal as a metal in a non-metallic phase included in the second plurality of particles and may comprise a metal in a metallic phase that is a different type of metal than the metal in a non-metallic phase included in the second plurality of particles (e.g., the first plurality of particles may comprise copper and zinc, and the second plurality of particles may comprise zinc oxide; the first plurality of particles may comprise copper and zinc, and the second plurality of particles may comprise zinc fluoride). Additionally or alternatively, the first plurality of particles may comprise a metal in a metallic phase that is the same type of metal as a metal in a non-metallic phase included in the second plurality of particles and the second plurality of particles may further comprise a different type of metal in a non-metallic phase (e.g., the first plurality of particles may comprise copper, and the second plurality of particles may comprise zinc oxide and magnesium oxide; the first plurality of particles may comprise copper, and the second plurality of particles may comprise zinc fluoride and magnesium fluoride; the first plurality of particles may comprise copper, and the second plurality of particles may comprise zinc oxide and magnesium fluoride).

In some embodiments, the electrode is exposed to a fluid that comprises a first plurality of particles comprising a metalloid in a metalloid phase and comprises a second plurality of particles comprising a metalloid in a non-metalloid phase. The metalloid in a non-metalloid phase may be a component of a halide salt (e.g., a fluoride salt) and/or a component of an oxide. The first plurality of particles may comprise a metalloid that does not form an alloy with a metal that is included in the electrode (e.g., the metalloid does not form an alloy with an alkali metal such as lithium). Additionally or alternatively, the first plurality of particles may comprise a metalloid that forms an alloy with a metal that is included in the electrode (e.g., the metalloid forms an alloy with an alkali metal such as lithium). The first plurality of particles may comprise a metalloid in a metalloid phase that is the same type of metalloid as metalloid in a non-metalloid phase included in the second plurality of particles (e.g., the first plurality of particles may comprise aluminum and the second plurality of particles may comprise alumina; the first plurality of particles may comprise an aluminum nanopowder and the second plurality of particles may comprise a fumed alumina powder; the first plurality of particles may comprise aluminum and the second plurality of particles may comprise aluminum fluoride). Additionally or alternatively, the first plurality of particles may comprise a metalloid that is a different type of

metalloid than a type of metalloid in a non-metalloid phase included in the second plurality of particles (e.g., the first plurality of particles may comprise antimony, and the second plurality of particles may comprise alumina; the first plurality of particles may comprise antimony, and the second plurality of particles may comprise aluminum fluoride). In some embodiments, the first
5 plurality of particles may comprise a metalloid in a metalloid phase that is the same type of metalloid as a metalloid in a non-metalloid phase included in the second plurality of particles and may comprise a metalloid in a metalloid phase that is a different type of metalloid than the metalloid in a non-metalloid phase included in the second plurality of particles (e.g., the first
10 plurality of particles may comprise alumina and antimony, and the second plurality of particles may comprise alumina; the first plurality of particles may comprise alumina and antimony, and the second plurality of particles may comprise aluminum fluoride). Additionally or alternatively, the first plurality of particles may comprise a metalloid in a metalloid phase that is the same type of metalloid as a metalloid in a non-metalloid phase included in the second plurality of particles and the second plurality of particles may further comprise a different type of metalloid in a non-
15 metalloid phase (e.g., the first plurality of particles may comprise aluminum, and the second plurality of particles may comprise alumina and an antimony oxide; the first plurality of particles may comprise aluminum, and the second plurality of particles may comprise aluminum fluoride and an antimony fluoride; the first plurality of particles may comprise aluminum, and the second plurality of particles may comprise alumina and an antimony fluoride).

20 Without wishing to be bound by any particular theory, it is believed that the combination of a first plurality of particles comprising a metal in a metallic phase or a metalloid in a metalloid phase and a second plurality of particles comprising a metal in a non-metallic phase or a metalloid in a non-metalloid phase may be particularly advantageous. Such combinations may be formulated to result in the formation of a protective structure (e.g., a protective structure
25 formed by a method described herein, a composite protective structure) with desired relative amounts of electronically conductive portions and electronically insulating portions. The electronically conductive portions are formed from the first plurality of particles, and from the metal or metalloid species in the second plurality of particles that react to form an alloy with a metal that is included in the electrode (e.g., an alloy comprising a metal that is included in the
30 electrode). The electronically insulating portions are formed from unreacted metal or metalloid species in the second plurality of particles, and from metal that is included in the electrode that

reacts with the component to which the metal or metalloid in the second plurality of particles is initially bound (e.g., an oxide of the metal that is included in the electrode, a fluoride salt of a metal that is included in the electrode).

In some embodiments, the fluid to which the electrode is exposed may comprise one or more protic solvent. That is, the fluid may comprise a solvent with a hydrogen atom bonded to an oxygen atom and/or a hydrogen atom bonded to a nitrogen atom. Non-limiting examples of protic solvents include ethanol, methanol, propanol, isopropanol, acetic acid, and ethylene glycol. Other protic solvents are also possible. In some embodiments, the protic solvent(s) may make up greater than or equal to 1 wt% of the fluid, greater than or equal to 2 wt% of the fluid, greater than or equal to 5 wt% of the fluid, greater than or equal to 10 wt% of the fluid, or greater than or equal to 15 wt% of the fluid. In some embodiments, the protic solvent(s) may make up less than or equal to 20 wt% of the fluid, less than or equal to 15 wt% of the fluid, less than or equal to 10 wt% of the fluid, less than or equal to 5 wt% of the fluid, or less than or equal to 2 wt% of the fluid. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 1 wt% and less than or equal to 20 wt%). Other ranges are also possible.

In some embodiments, the fluid may comprise one or more aprotic solvents. The aprotic solvent(s) may include, for example, polar aprotic solvents (e.g., pyridine, dimethyl carbonate, propylene glycol mono-methyl ether acetate, dimethyl sulfoxide, N,N'-dimethyl acetamide, methyl ethyl ketone, methyl isobutyl ketone, diethyl ether, tetrahydrofuran, 2-methyl tetrahydrofuran, diethoxyethane, 1,3-dioxolane, diethyl carbonate, ethyl methyl carbonate, methyl formate, butyl acetate, methyl acetate, acetonitrile, nitromethane) and/or nonpolar aprotic solvents (e.g., n-hexane, toluene, n-butane, n-heptane). Other aprotic solvents are also possible. In some embodiments, the aprotic solvent(s) may make up greater than or equal to 50 wt% of the fluid, greater than or equal to 75 wt% of the fluid, greater than or equal to 90 wt% of the fluid, or greater than or equal to 95 wt% of the fluid. In some embodiments, the aprotic solvent(s) may make up less than or equal to 99 wt% of the fluid, less than or equal to 95 wt% of the fluid, less than or equal to 90 wt% of the fluid, or less than or equal to 75 wt% of the fluid. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 50 wt% of the fluid and less than or equal to 99 wt% of the fluid). Other ranges are also possible.

In some embodiments, a fluid may comprise at least one protic solvent and at least one aprotic solvent. In such embodiments, the aprotic solvent(s) may make up any suitable wt% of

the solvents present. In some embodiments, the protic solvent(s) may make up greater than or equal to 1 wt% of the solvents present, greater than or equal to 2 wt% of the solvents present, greater than or equal to 5 wt% of the solvents present, greater than or equal to 10 wt% of the solvents present, or greater than or equal to 15 wt% of the solvents present. In some
5 embodiments, the protic solvent(s) may make up less than or equal to 20 wt% of the solvents present, less than or equal to 15 wt% of the solvents present, less than or equal to 10 wt% of the solvents present, less than or equal to 5 wt% of the solvents present, or less than or equal to 2 wt% of the solvents present. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 1 wt% and less than or equal to 20 wt%). Other ranges are also
10 possible.

In some embodiments, a method for forming a protective structure may comprise heating an electrode or protected electrode (e.g., after exposing the electrode to the fluid). Heating may comprise placing the electrode or protected electrode structure in an environment where the ambient temperature is greater than or equal to 60 °C, greater than or equal to 80 °C, greater than
15 or equal to 100 °C, greater than or equal to 120 °C, greater than or equal to 140 °C, greater than or equal to 160 °C, greater than or equal to 180 °C, greater than or equal to 200 °C, or greater than or equal to 220 °C. Heating may comprise placing the electrode or protected electrode structure in an environment where the ambient temperature is less than or equal to 240 °C, less than or equal to 220 °C, less than or equal to 200 °C, less than or equal to 180 °C, less than or
20 equal to 160 °C, less than or equal to 140 °C, less than or equal to 120 °C, less than or equal to 100 °C, or less than or equal to 80 °C. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 60 °C and less than or equal to 240 °C). Other ranges are also possible.

Heating may be accomplished at any suitable pressure. In some embodiments, an
25 electrode or protected electrode may be heated while subject to a reduced (e.g., vacuum) pressure. The reduced pressure may be less than or equal to 760 torr, less than or equal to 700 torr, less than or equal to 500 torr, less than or equal to 200 torr, less than or equal to 100 torr, less than or equal to 50 torr, less than or equal to 20 torr, less than or equal to 10 torr, less than or equal to 5 torr, less than or equal to 2 torr, less than or equal to 1 torr, less than or equal to 0.5
30 torr, less than or equal to 0.2 torr, less than or equal to 0.1 torr, less than or equal to 0.05 torr, or less than or equal to 0.02 torr. The reduced pressure may be greater than or equal to 0.01 torr,

greater than or equal to 0.02 torr, greater than or equal to 0.05 torr, greater than or equal to 0.1 torr, greater than or equal to 0.2 torr, greater than or equal to 0.5 torr, greater than or equal to 1 torr, greater than or equal to 2 torr, greater than or equal to 5 torr, greater than or equal to 10 torr, greater than or equal to 20 torr, greater than or equal to 50 torr, greater than or equal to 100 torr, greater than or equal to 200 torr, greater than or equal to 500 torr, or greater than or equal to 700 torr. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 0.01 torr and less than or equal to 760 torr). Other ranges are also possible.

As described above, in some embodiments a protective structure may be formed on an electrode. In some embodiments, the electrode may be an anode. In some embodiments, the electrode comprises an alkali metal. The alkali metal may be lithium (e.g., lithium metal), such as lithium foil, lithium deposited onto a conductive substrate, and lithium alloys (e.g., lithium-aluminum alloys and lithium-tin alloys). Lithium can be contained as one film or as several films, optionally separated. Suitable lithium alloys for use in the aspects described herein can include alloys of lithium and aluminum, magnesium, silicon (silicon), indium, and/or tin.

In some embodiments, the electrode contains at least 50 wt% lithium. In some cases, the electrode contains at least 75 wt%, at least 90 wt%, at least 95 wt%, or at least 99 wt% lithium. In some embodiments, the anode active material contains at least 50 wt% lithium. In some cases, the anode active material contains at least 75 wt%, at least 90 wt%, at least 95 wt%, or at least 99 wt% lithium.

In some embodiments, the electrode is an electrode from which a lithium ion is liberated during discharge and into which the lithium ion is integrated (e.g., intercalated) during charge. In some embodiments, the electrode is a lithium intercalation compound (e.g., a compound that is capable of reversibly inserting lithium ions at lattice sites and/or interstitial sites). In some embodiments, the electrode comprises carbon. In certain cases, the electrode is or comprises a graphitic material (e.g., graphite). A graphitic material generally refers to a material that comprises a plurality of layers of graphene (e.g., layers comprising carbon atoms arranged in a hexagonal lattice). Adjacent graphene layers are typically attracted to each other via van der Waals forces, although covalent bonds may be present between one or more sheets in some cases. In some cases, the carbon-comprising material of the electrode is or comprises coke (e.g., petroleum coke). In certain embodiments, the electrode comprises silicon, lithium, and/or any

alloys of combinations thereof. In certain embodiments, the electrode comprises lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$, also referred to as "LTO"), tin-cobalt oxide, or any combinations thereof.

In some embodiments, a surface of the electrode (e.g., a surface to be exposed to a fluid, a surface directly adjacent a protective structure) may be passivated. Without wishing to be
5 bound by theory, electrode surfaces that are passivated are surfaces that have undergone a chemical reaction to form a layer that is less reactive (e.g., with an ambient atmosphere, with a fluid, with an electrolyte) than material that is present in the bulk of the electrode. One method of passivating an electrode surface is to expose the electrode to a plasma comprising CO_2 and/or SO_2 to form a CO_2 - or SO_2 -induced layer. Certain inventive methods and articles may comprise
10 passivating an electrode by exposing it to CO_2 and/or SO_2 , or an electrode with a surface that has been passivated by exposure to CO_2 and/or SO_2 . Such exposure may form a porous passivation layer on the electrode (e.g., a CO_2 - or SO_2 -induced layer).

In some embodiments, an electrode or protected electrode structure as described herein has not been cycled, or has been cycled a minimal number of times. For instance, the electrode
15 or protected electrode structure may have been cycled fewer than 10 times, 5 times, or 2 times.

In some embodiments, an electrode or protected electrode structure as described herein may be one component of an electrochemical cell. The electrochemical cell may comprise additional components commonly associated with electrochemical cells (e.g., electrolytes, separators, second electrodes, current collectors), some of which are described in more detail
20 below.

The electrolytes used in electrochemical or battery cells can function as a medium for the storage and transport of ions, and in the special case of solid electrolytes and gel electrolytes, these materials may additionally function as a separator between the anode and the cathode. Any liquid, solid, or gel material capable of storing and transporting ions may be used, so long as the
25 material facilitates the transport of ions (e.g., lithium ions) between the anode and the cathode. The electrolyte is electronically non-conductive to prevent short circuiting between the anode and the cathode. In some embodiments, the electrolyte may comprise a non-solid electrolyte.

Suitable non-aqueous electrolytes may include organic electrolytes comprising one or more materials selected from the group consisting of liquid electrolytes, gel polymer electrolytes,
30 and solid polymer electrolytes. Examples of non-aqueous electrolytes for lithium batteries are described by Dorniney in Lithium Batteries, New Materials, Developments and Perspectives,

Chapter 4, pp. 137-165, Elsevier, Amsterdam (1994). Examples of gel polymer electrolytes and solid polymer electrolytes are described by Alamgir et al. in *Lithium Batteries, New Materials, Developments and Perspectives*, Chapter 3, pp. 93-136, Elsevier, Amsterdam (1994).

Heterogeneous electrolyte compositions that can be used in batteries described herein are
5 described in U.S. Patent Application Serial No. 12/312,764, filed May 26, 2009 and entitled
“Separation of Electrolytes,” by Mikhaylik et al., which is incorporated herein by reference in its
entirety.

In some embodiments, an electrolyte may be used in the electrochemical cells described
herein. Generally, the choice of electrolyte will depend upon the chemistry of the
10 electrochemical cell, and, in particular, the species of ion that is to be transported between
electrodes in the electrochemical cell. Suitable electrolytes can comprise, in some embodiments,
one or more ionic electrolyte salts to provide ionic conductivity and one or more liquid
electrolyte solvents. Examples of useful non-aqueous electrolyte solvents include, but are not
limited to, non-aqueous organic solvents, such as, for example, N-methyl acetamide, acetonitrile,
15 acetals, ketals, esters, carbonates, sulfones, sulfites, sulfolanes, aliphatic ethers, cyclic ethers,
glymes, polyethers, phosphate esters, siloxanes, dioxolanes (e.g., 1,3-dioxolane), N-
alkylpyrrolidones, bis(trifluoromethanesulfonyl)imide, substituted forms of the foregoing, and
blends thereof. Fluorinated derivatives of the foregoing are also useful as liquid electrolyte
solvents.

20 In some cases, aqueous solvents can be used as electrolytes (e.g., for lithium cells).
Aqueous solvents can include water, which can contain other components such as ionic salts. In
some embodiments, the electrolyte can include species such as lithium hydroxide, or other
species rendering the electrolyte basic, so as to reduce the concentration of hydrogen ions in the
electrolyte.

25 Liquid electrolyte solvents can also be useful as plasticizers for gel polymer electrolytes,
i.e., electrolytes comprising one or more polymers forming a semi-solid network. Examples of
useful gel polymer electrolytes include, but are not limited to, those comprising one or more
polymers selected from the group consisting of polyethylene oxides, polypropylene oxides,
polyacrylonitriles, polysiloxanes, polyimides, polyphosphazenes, polyethers, sulfonated
30 polyimides, perfluorinated membranes (NAFION resins), polydivinyl polyethylene glycols,
polyethylene glycol diacrylates, polyethylene glycol dimethacrylates, polysulfones,

polyethersulfones, derivatives of the foregoing, copolymers of the foregoing, crosslinked and network structures of the foregoing, and blends of the foregoing, and optionally, one or more plasticizers. In some embodiments, a gel polymer electrolyte comprises between 10-20%, 20-40%, between 60-70%, between 70-80%, between 80-90%, or between 90-95% of a
5 heterogeneous electrolyte by volume. The percentages above should be understood to refer to the percentage of the volume of the heterogeneous electrolyte that is occupied by a gel polymer electrolyte.

In some embodiments, one or more solid polymers can be used to form an electrolyte. Examples of useful solid polymer electrolytes include, but are not limited to, those comprising
10 one or more polymers selected from the group consisting of polyethers, polyethylene oxides, polypropylene oxides, polyimides, polyphosphazenes, polyacrylonitriles, polysiloxanes, derivatives of the foregoing, copolymers of the foregoing, crosslinked and network structures of the foregoing, and blends of the foregoing.

In addition to electrolyte solvents, gelling agents, and polymers as known in the art for
15 forming electrolytes, the electrolyte may further comprise one or more ionic electrolyte salts, also as known in the art, to increase the ionic conductivity.

The electrolyte can comprise one or more ionic electrolyte salts to provide ionic conductivity and one or more liquid electrolyte solvents, gel polymer materials, polymer materials, or liquid-containing materials. In some embodiments, one or more lithium salts (e.g.,
20 LiSCN, LiBr, LiI, LiClO₄, LiAsF₆, LiSO₃CF₃, LiSO₃CH₃, LiBF₄, LiB(Ph)₄, LiPF₆, LiC(SO₂CF₃)₃, and LiN(SO₂CF₃)₂) can be included. Other electrolyte salts that may be useful include lithium polysulfides (Li₂S_x), and lithium salts of organic ionic polysulfides (LiS_xR)_n, where x is an integer from 1 to 20, n is an integer from 1 to 3, and R is an organic group, and those disclosed in U.S. Patent No. 5,538,812 to Lee et al. A range of concentrations of the ionic
25 lithium salts in the solvent may be used such as from about 0.2 m to about 2.0 m (m is moles/kg of solvent). In some embodiments, a concentration in the range between about 0.5 m to about 1.5 m is used.

In some embodiments, electrochemical cells may further comprise a separator interposed between the protected electrode structure and a second electrode. In some embodiments, one or
30 more cell components described above (such as, e.g., a first insulating layer, a second insulating layer, etc.) may be a separator. The separator may be a solid non-conductive or insulative

material which separates or insulates the anode and the cathode from each other preventing short circuiting, and which permits the transport of ions between the anode and the cathode. In some embodiments, the porous separator may be permeable to the electrolyte.

The pores of the separator or separators may be partially or substantially filled with electrolyte. Separators may be supplied as porous free standing films which are interleaved with the anodes and the cathodes during the fabrication of cells. Alternatively, the porous separator layer may be applied directly to the surface of one of the electrodes, for example, as described in PCT Publication No. WO 99/33125 to Carlson et al. and in U.S. Patent No. 5,194,341 to Bagley et al.

A variety of separator materials are known in the art. Examples of suitable solid porous separator materials include, but are not limited to, polyolefins, such as, for example, polyethylenes (e.g., SETELA™ made by Tonen Chemical Corp) and polypropylenes, glass fiber filter papers, and ceramic materials. For example, in some embodiments, the separator comprises a microporous polyethylene film. Further examples of separators and separator materials suitable for use according to certain embodiments are those comprising a microporous xerogel layer, for example, a microporous pseudo-boehmite layer, which may be provided either as a free standing film or by a direct coating application on one of the electrodes, as described in U.S. Patent Nos. 6,153,337 and 6,306,545 by Carlson et al. of the common assignee. Solid electrolytes and gel electrolytes may also function as a separator in addition to their electrolyte function.

In some embodiments, an electrochemical cell comprising a protected electrode structure as described herein may further comprise a second electrode, such as a cathode. The second electrode may comprise a lithium intercalation compound (e.g., a compound that is capable of reversibly inserting lithium ions at lattice sites and/or interstitial sites). In certain cases, the second electrode comprises a layered oxide. A layered oxide generally refers to an oxide having a lamellar structure (e.g., a plurality of sheets, or layers, stacked upon each other). Non-limiting examples of suitable layered oxides include lithium cobalt oxide (LiCoO_2), lithium nickel oxide (LiNiO_2), and lithium manganese oxide (LiMnO_2). In some embodiments, the layered oxide is lithium nickel manganese cobalt oxide ($\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$, also referred to as “NMC” or “NCM”). In some such embodiments, the sum of x, y, and z is 1. For example, a non-limiting example of a suitable NMC compound is $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$. In some embodiments, the layered oxide is

lithium nickel cobalt aluminum oxide ($\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$, also referred to as “NCA”). In some such embodiments, the sum of x , y , and z is 1. For example, a non-limiting example of a suitable NCA compound is $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$. In certain embodiments, the second electrode comprises a transition metal polyanion oxide (e.g., a compound comprising a transition metal, an oxygen, and/or an anion having a charge with an absolute value greater than 1). A non-limiting example of a suitable transition metal polyanion oxide is lithium iron phosphate (LiFePO_4 , also referred to as “LFP”). Another non-limiting example of a suitable transition metal polyanion oxide is lithium manganese iron phosphate ($\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$, also referred to as “LMFP”). A non-limiting example of a suitable LMFP compound is $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$. In some embodiments, the second electrode comprises a spinel (e.g., a compound having the structure AB_2O_4 , where A can be Li, Mg, Fe, Mn, Zn, Cu, Ni, Ti, or Si, and B can be Al, Fe, Cr, Mn, or V). A non-limiting example of a suitable spinel is lithium manganese oxide (LiMn_2O_4 , also referred to as “LMO”). Another non-limiting example is lithium manganese nickel oxide ($\text{LiNi}_x\text{M}_{2-x}\text{O}_4$, also referred to as “LMNO”). A non-limiting example of a suitable LMNO compound is $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. In certain cases, the second electrode comprises $\text{Li}_{1.14}\text{Mn}_{0.42}\text{Ni}_{0.25}\text{Co}_{0.29}\text{O}_2$ (“HC-MNC”), lithium carbonate (Li_2CO_3), lithium carbides (e.g., Li_2C_2 , Li_4C , Li_6C_2 , Li_8C_3 , Li_6C_3 , Li_4C_3 , Li_4C_5), vanadium oxides (e.g., V_2O_5 , V_2O_3 , V_6O_{13}), and/or vanadium phosphates (e.g., lithium vanadium phosphates, such as $\text{Li}_3\text{V}_2(\text{PO}_4)_3$), or any combination thereof.

In some embodiments, the second electrode comprises a conversion compound. For instance, the second electrode may be a lithium conversion electrode/cathode. It has been recognized that a cathode comprising a conversion compound may have a relatively large specific capacity. Without wishing to be bound by a particular theory, a relatively large specific capacity may be achieved by utilizing all possible oxidation states of a compound through a conversion reaction in which more than one electron transfer takes place per transition metal (e.g., compared to 0.1-1 electron transfer in intercalation compounds). Suitable conversion compounds include, but are not limited to, transition metal oxides (e.g., Co_3O_4), transition metal hydrides, transition metal sulfides, transition metal nitrides, and transition metal fluorides (e.g., CuF_2 , FeF_2 , FeF_3). A transition metal generally refers to an element whose atom has a partially filled d sub-shell (e.g., Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Rf, Db, Sg, Bh, Hs).

In some cases, the second electrode may comprise a material that is doped with one or more dopants to alter the electrical properties (e.g., electrical conductivity) of the electrode active material. Non-limiting examples of suitable dopants include aluminum, niobium, silver, and zirconium.

5 In certain embodiments, the second electrode can comprise sulfur. In some
embodiments, the second electrode can comprise electrode active sulfur-containing materials.
“Electroactive sulfur-containing materials,” as used herein, refers to electrode active materials
which comprise the element sulfur in any form, wherein the electrochemical activity involves the
oxidation or reduction of sulfur atoms or moieties. As an example, the electrode active sulfur-
10 containing material may comprise elemental sulfur (e.g., S₈). In some embodiments, the
electrode active sulfur-containing material comprises a mixture of elemental sulfur and a sulfur-
containing polymer. Thus, suitable electrode active sulfur-containing materials may include, but
are not limited to, elemental sulfur, sulfides or polysulfides (e.g., of alkali metals) which may be
organic or inorganic, and organic materials comprising sulfur atoms and carbon atoms, which
15 may or may not be polymeric. Suitable organic materials include, but are not limited to, those
further comprising heteroatoms, conductive polymer segments, composites, and conductive
polymers. In some embodiments, an electrode active sulfur-containing material within a second
electrode (e.g., a cathode) comprises at least about 40 wt% sulfur. In some cases, the electrode
active sulfur-containing material comprises at least about 50 wt%, at least about 75 wt%, or at
20 least about 90 wt% sulfur.

Examples of sulfur-containing polymers include those described in: U.S. Patent Nos.
5,601,947 and 5,690,702 to Skotheim et al.; U.S. Patent Nos. 5,529,860 and 6,117,590 to
Skotheim et al.; U.S. Patent No. 6,201,100 issued Mar. 13, 2001, to Gorkovenko et al., and PCT
Publication No. WO 99/33130. Other suitable electrode active sulfur-containing materials
25 comprising polysulfide linkages are described in U.S. Patent No. 5,441,831 to Skotheim et al.;
U.S. Patent No. 4,664,991 to Perichaud et al., and in U.S. Patent Nos. 5,723,230, 5,783,330,
5,792,575 and 5,882,819 to Naoi et al. Still further examples of electrode active sulfur-
containing materials include those comprising disulfide groups as described, for example in, U.S.
Patent No. 4,739,018 to Armand et al.; U.S. Patent Nos. 4,833,048 and 4,917,974, both to De
30 Jonghe et al.; U.S. Patent Nos. 5,162,175 and 5,516,598, both to Visco et al.; and U.S. Patent
No. 5,324,599 to Oyama et al.

In some embodiments, the use of certain protected electrode structures described herein may result in improved capacity after repeated cycling of the electrochemical cell. For example, in some embodiments, after alternatively discharging and charging the cell three times, the cell exhibits at least about 50%, at least about 80%, at least about 90%, or at least about 95% of the cell's initial capacity at the end of the third cycle. In some cases, after alternatively discharging and charging the cell ten times, the cell exhibits at least about 50%, at least about 80%, at least about 90%, or at least about 95% of the cell's initial capacity at the end of the tenth cycle. In still further cases, after alternatively discharging and charging the cell twenty-five times, the cell exhibits at least about 50%, at least about 80%, at least about 90%, or at least about 95% of the cell's initial capacity at the end of the twenty-fifth cycle.

EXAMPLES

The examples presented herein describe the formation of protected electrode structures on lithium electrodes.

Unless otherwise specified, the following procedure was followed in a dry room. Lithium which had been formed by vapor deposition and then passivated by CO₂ was dipped into a bath solution (shown in Table 1) for approximately 10 seconds and then withdrawn. Then, the sample was held in ambient air for a time period shown in Table 1, by which point the solvent had fully evaporated. During this time period, the lithium surface became darker and curled away from the coating for Examples 1-3. Next, the sample was placed into a vacuum oven preset at 130 °C and held at this temperature for a time period shown in Table 1. After this step, the sample was unloaded and allowed to cool to room temperature under dry air. After the protective structure had been formed by the above process, the sample was imaged using scanning electron microscopy (SEM) and analyzed using X-ray diffraction. Example 6 only was stored under Argon for two months prior to X-ray diffraction analysis.

Table 1. Bath solutions.

Example	Salt or particle (concentration)	Solvent	Evaporation time	Heating time
Example 1	SbF ₃ (0.5 M)	10 vol% methanol; 90 vol% dimethyl	3 minutes	10 minutes

		carbonate		
Example 2	SnF ₂ (0.5 M)	Pyridine	3 minutes	10 minutes
Example 3	SnF ₂ (0.33 M); SbF ₃ (0.17 M)	25 vol% methanol; 75 vol% pyridine	3 minutes	10 minutes
Example 4	ZnO nanoparticles (4 wt%)	6.25 wt% ethanol; 93.75 wt% dimethyl carbonate	3 minutes	30 minutes
Example 5	Colloidal graphite (5 wt%)	47 wt% n-heptane, 16 wt% propane, 16 wt% butane, 16 wt% 2-propanol, and 5 wt% toluene	1 minute	60 minutes
Example 6	Al ₂ O ₃ nanoparticles (20 wt%)	Isopropanol	3 minutes	60 minutes

SEM images of the protective structures showed that they formed particulate films (see FIGs. 3A-3B for Example 1; FIGs. 4A-4B for Example 2; FIGs. 5A-5B for Example 3; FIGs. 6A-6C for Example 4; FIGs. 7A-7B for Example 5; FIGs. 8A-8B for Example 6).

5 X-ray diffraction data from the protective structures indicated that they comprised a variety of compounds, including lithium alloys, fluoride salts, oxides, and elemental carbon. Although not detected by X-ray diffraction, lithium fluoride is expected to have formed from a metathesis reaction between the lithium and the metal fluoride salt in Examples 1-3, and lithium oxide is expected to have formed from a metathesis reaction between the lithium and the metal
10 oxide particles in Examples 4 and 6. Table 2 shows the composition of each protective structure calculated based on X-ray diffraction peak intensities.

Table 2. Protective structure compositions.

Example	Protective structure composition
Example 1	42 wt% Li ₃ Sb; 54 wt% SbF ₃ ; 4 wt% Sb
Example 2	90 wt% Li ₄ Sn; 10 wt% SnO ₂
Example 3	Comprises Li-Sn and Li-Sb alloys

Example 4	36 wt% LiZn; 25 wt% LiZn ₁₃ ; 39 wt% ZnO
Example 5	2 wt% Li ₃ C ₂₄ ; 98 wt% graphite
Example 6	3.7 wt% LiAl ₃ , 9.9 wt% LiAlO ₂ , 86.4 wt% Al ₂ O ₃

While several embodiments of the present invention have been described and illustrated herein, those of ordinary skill in the art will readily envision a variety of other means and/or structures for performing the functions and/or obtaining the results and/or one or more of the advantages described herein, and each of such variations and/or modifications is deemed to be within the scope of the present invention. More generally, those skilled in the art will readily appreciate that all parameters, dimensions, materials, and configurations described herein are meant to be exemplary and that the actual parameters, dimensions, materials, and/or configurations will depend upon the specific application or applications for which the teachings of the present invention is/are used. Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention described herein. It is, therefore, to be understood that the foregoing embodiments are presented by way of example only and that, within the scope of the appended claims and equivalents thereto, the invention may be practiced otherwise than as specifically described and claimed. The present invention is directed to each individual feature, system, article, material, kit, and/or method described herein. In addition, any combination of two or more such features, systems, articles, materials, kits, and/or methods, if such features, systems, articles, materials, kits, and/or methods are not mutually inconsistent, is included within the scope of the present invention.

All definitions, as defined and used herein, should be understood to control over dictionary definitions, definitions in documents incorporated by reference, and/or ordinary meanings of the defined terms.

The indefinite articles “a” and “an,” as used herein in the specification and in the claims, unless clearly indicated to the contrary, should be understood to mean “at least one.”

The phrase “and/or,” as used herein in the specification and in the claims, should be understood to mean “either or both” of the elements so conjoined, i.e., elements that are conjunctively present in some cases and disjunctively present in other cases. Multiple elements

listed with “and/or” should be construed in the same fashion, i.e., “one or more” of the elements so conjoined. Other elements may optionally be present other than the elements specifically identified by the “and/or” clause, whether related or unrelated to those elements specifically identified. Thus, as a non-limiting example, a reference to “A and/or B”, when used in
5 conjunction with open-ended language such as “comprising” can refer, in one embodiment, to A only (optionally including elements other than B); in another embodiment, to B only (optionally including elements other than A); in yet another embodiment, to both A and B (optionally including other elements); etc.

As used herein in the specification and in the claims, “or” should be understood to have
10 the same meaning as “and/or” as defined above. For example, when separating items in a list, “or” or “and/or” shall be interpreted as being inclusive, i.e., the inclusion of at least one, but also including more than one, of a number or list of elements, and, optionally, additional unlisted items. Only terms clearly indicated to the contrary, such as “only one of” or “exactly one of,” or, when used in the claims, “consisting of,” will refer to the inclusion of exactly one element of a
15 number or list of elements. In general, the term “or” as used herein shall only be interpreted as indicating exclusive alternatives (i.e. “one or the other but not both”) when preceded by terms of exclusivity, such as “either,” “one of,” “only one of,” or “exactly one of.” “Consisting essentially of,” when used in the claims, shall have its ordinary meaning as used in the field of patent law.

As used herein in the specification and in the claims, the phrase “at least one,” in
20 reference to a list of one or more elements, should be understood to mean at least one element selected from any one or more of the elements in the list of elements, but not necessarily including at least one of each and every element specifically listed within the list of elements and not excluding any combinations of elements in the list of elements. This definition also allows
25 that elements may optionally be present other than the elements specifically identified within the list of elements to which the phrase “at least one” refers, whether related or unrelated to those elements specifically identified. Thus, as a non-limiting example, “at least one of A and B” (or, equivalently, “at least one of A or B,” or, equivalently “at least one of A and/or B”) can refer, in one embodiment, to at least one, optionally including more than one, A, with no B present (and
30 optionally including elements other than B); in another embodiment, to at least one, optionally including more than one, B, with no A present (and optionally including elements other than A);

in yet another embodiment, to at least one, optionally including more than one, A, and at least one, optionally including more than one, B (and optionally including other elements); etc.

It should also be understood that, unless clearly indicated to the contrary, in any methods claimed herein that include more than one step or act, the order of the steps or acts of the method
5 is not necessarily limited to the order in which the steps or acts of the method are recited.

In the claims, as well as in the specification above, all transitional phrases such as “comprising,” “including,” “carrying,” “having,” “containing,” “involving,” “holding,” “composed of,” and the like are to be understood to be open-ended, i.e., to mean including but not limited to. Only the transitional phrases “consisting of” and “consisting essentially of” shall
10 be closed or semi-closed transitional phrases, respectively, as set forth in the United States Patent Office Manual of Patent Examining Procedures, Section 2111.03.

What is claimed is:

CLAIMS

1. A protected electrode structure, comprising:
5 an electrode comprising an alkali metal; and
a composite protective structure directly adjacent the electrode, wherein the composite protective structure comprises:
an alloy comprising the alkali metal; and
an oxide of the alkali metal.
10
2. A method of forming a protected electrode, comprising:
exposing an electrode comprising an alkali metal to a liquid comprising a plurality of particles, wherein the plurality of particles comprises at least one of a metal-containing species and a metalloid-containing species; and
15 forming a composite protective structure on the electrode, wherein the composite protective structure comprises an alloy comprising the alkali metal.
3. A protected electrode structure, comprising:
an electrode comprising an alkali metal; and
20 a composite protective structure directly adjacent the electrode, wherein the composite protective structure comprises:
an alloy comprising the alkali metal; and
a fluoride salt of the alkali metal,
wherein the fluoride salt of the alkali metal makes up greater than or equal to 0.1 wt% of
25 the composite protective structure.
4. A method of forming a protected electrode, comprising:
exposing an electrode comprising an alkali metal to a liquid comprising a metal fluoride salt or a metalloid fluoride salt; and

forming a composite protective structure on the electrode, wherein the composite protective structure comprises an alloy comprising the alkali metal and a fluoride salt of the alkali metal.

- 5 5. A protected electrode structure, comprising:
an electrode comprising an alkali metal; and
a protective structure directly adjacent the electrode, wherein the protective structure comprises elemental carbon and intercalated ions of the alkali metal.
- 10 6. A method of forming a protected electrode, comprising:
exposing an electrode comprising an alkali metal to a liquid comprising a plurality of particles, wherein the plurality of particles comprises elemental carbon; and
forming a protective structure on the electrode, wherein the protective structure comprises the elemental carbon.
- 15 7. A method or a protected electrode structure as in any preceding claim, wherein the composite protective structure comprises pores.
8. A method or a protected electrode structure as in any preceding claim, wherein the
20 composite protective structure comprises particles.
9. A method or a protected electrode structure as in any preceding claim, wherein the composite protective structure is substantially impermeable to an electrolyte.
- 25 10. A method or a protected electrode structure as in any preceding claim, wherein the composite protective structure further comprises a second oxide.
11. A method or a protected electrode structure as in any preceding claim, wherein the composite protective structure comprises particles having a core-shell structure.

12. A method or a protected electrode structure as in claim 11, wherein the alloy forms the shell of the core-shell structure.
13. A method or a protected electrode structure as in any preceding claim, wherein the composite protective structure forms an interpenetrating network structure.
14. A method or a protected electrode structure as in any preceding claim, wherein the alkali metal comprises lithium.
15. A method or a protected electrode structure as in any preceding claim, wherein the metal-containing species comprises a metal oxide.
16. A method or a protected electrode structure as in any preceding claim, wherein the metalloid-containing species comprises a metalloid oxide.
17. A method or a protected electrode structure as in any preceding claim, wherein the metal-containing species comprises at least one of Sn, Zn, In, Al, Mg, Ga, Ag, Cd, Pb, and Bi.
18. A method or a protected electrode structure as in any preceding claim, wherein the metalloid-containing species comprises at least one of Sb, Si, Ge, and As.
19. A method or a protected electrode structure as in any preceding claim, wherein the alloy comprises at least one of Sn, Zn, In, Al, Mg, Ga, Ag, Cd, Pb, Bi, Sb, Si, Ge, and As.
20. A method or a protected electrode structure as in any preceding claim, wherein the plurality of particles has an average size of greater than or equal to 5 nm and less than or equal to 2 microns.
21. A method or a protected electrode structure as in any preceding claim, wherein the oxide of the alkali metal makes up greater than or equal to 0.1 wt% of the protective structure and less than or equal to 70 wt% of the protective structure.

22. A method or a protected electrode structure as in any preceding claim, wherein the oxide of the alkali metal makes up greater than or equal to 10 wt% of the protective structure and less than or equal to 50 wt% of the protective structure.

5

23. A method or a protected electrode structure as in any preceding claim, wherein the fluoride salt of the alkali metal makes up greater than or equal to 10 wt% of the protective structure and less than or equal to 50 wt% of the protective structure.

10 24. A method or a protected electrode structure as in any preceding claim, wherein the elemental carbon comprises at least one of graphite, carbon nanotubes, carbon nanofibers, and graphene oxide.

15 25. A method or a protected electrode structure as in any preceding claim, wherein the liquid comprises a protic solvent.

26. A method or a protected electrode structure as in any preceding claim, wherein the liquid comprises at least one of ethanol, methanol, and isopropanol.

20 27. A method or a protected electrode structure as in any preceding claim, wherein the liquid comprises an aprotic solvent.

25 28. A method or a protected electrode structure as in any preceding claim, wherein the liquid comprises at least one of dimethyl carbonate, n-hexane, pyridine, propylene glycol mono-methyl ether acetate, dimethyl sulfoxide, N,N'-dimethyl acetamide, methyl ethyl ketone, methyl isobutyl ketone, diethyl ether, tetrahydrofuran, 2-methyl tetrahydrofuran, diethoxyethane, 1,3-dioxolane, diethyl carbonate, ethyl methyl carbonate, methyl formate, butyl acetate, methyl acetate, acetonitrile, nitromethane

30 29. A method or a protected electrode structure as in any preceding claim, wherein a surface of the electrode is passivated.

30. A method or a protected electrode structure as in any preceding claim, wherein a surface of the electrode is passivated due to prior exposure to CO₂.
- 5 31. A method as in any preceding claim, further comprising heating the protected electrode.
32. A method as in claim 31, wherein the protected electrode structure is held at a reduced pressure during heating.
- 10 33. An electrochemical cell comprising the protected electrode structure of any preceding claim.
34. A method or a protected electrode structure as in any preceding claim, wherein the protected electrode has not been cycled.
- 15 35. A method or a protected electrode structure as in any preceding claim, wherein the protective structure has a thickness of at least 20 nm and less than or equal to 5 microns.
36. A method or protected electrode as in any preceding claim, wherein the composite
20 protective structure further comprises a metal-containing species in a metallic phase or a metalloid-containing species in a metalloid phase.
37. A method or protected electrode as in claim 36, wherein the metal-containing species in the metallic phase comprises a metal that does not form an alloy with the alkali metal.
- 25 38. A method or protected electrode structure as in any one of claims 36-37, wherein the metal-containing species in the metallic phase comprises at least one of Cu, Ni, and Fe.
39. A method or protected electrode as in any preceding claim, wherein the particles
30 comprise nanoparticles.

40. A method or protected electrode as in claim 39, wherein the particles are metal oxide particles or metalloid oxide particles.

41. A method or protected electrode as in claim 40, wherein the particles are metal particles
5 or metalloid particles.

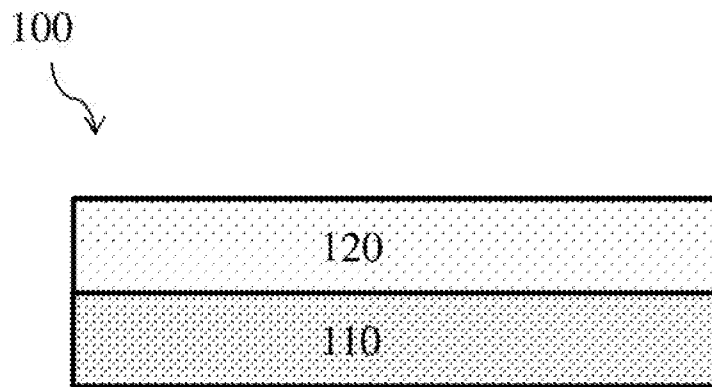


FIG. 1

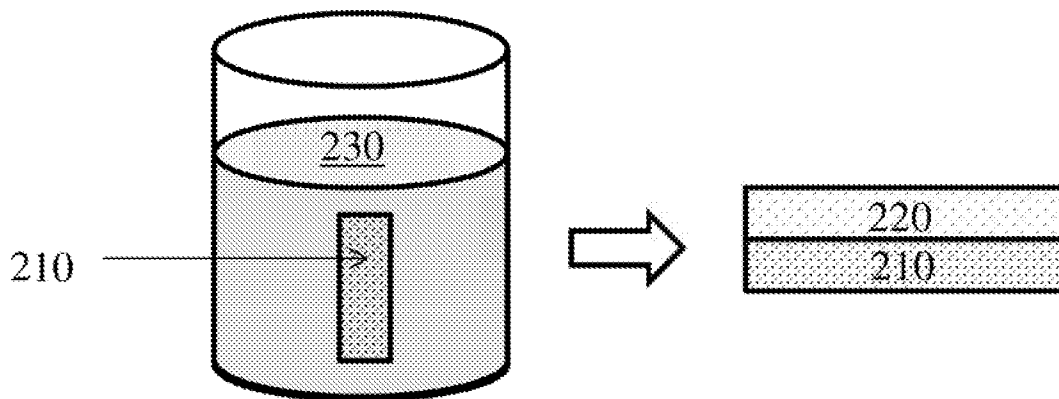


FIG. 2

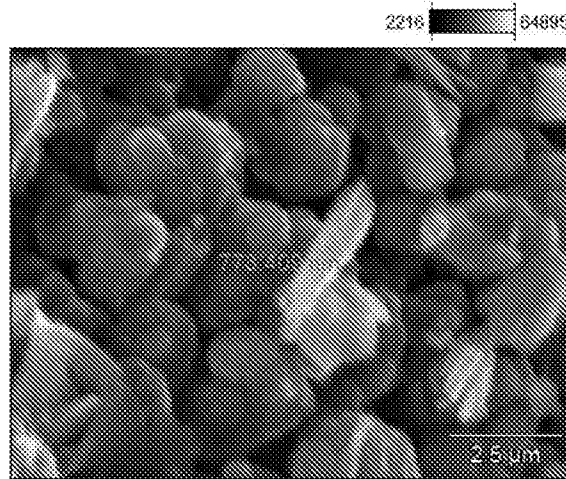


FIG. 3A

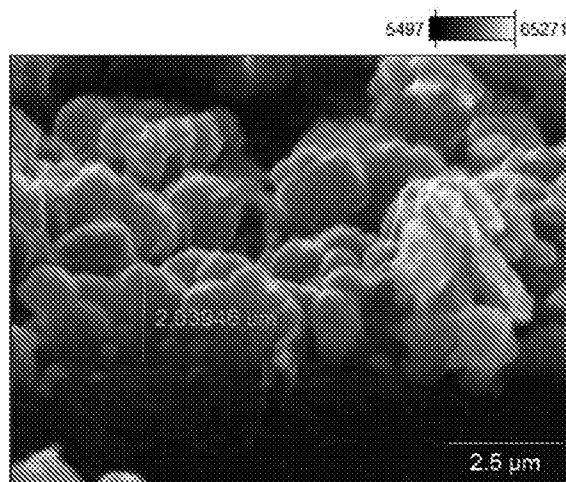


FIG. 3B

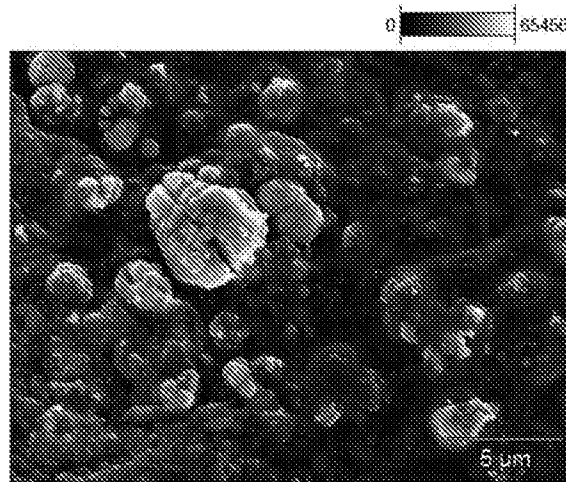


FIG. 4A

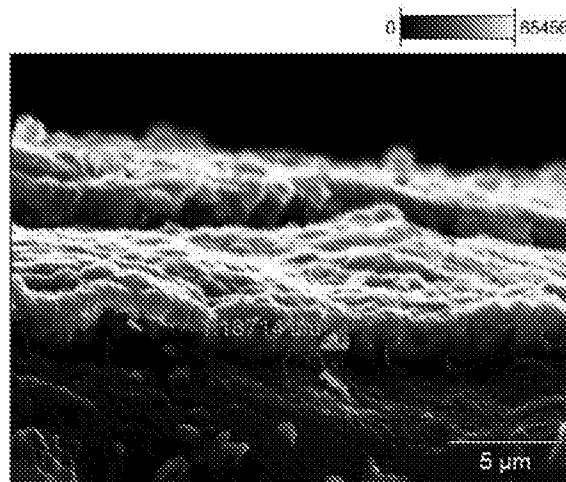


FIG. 4B

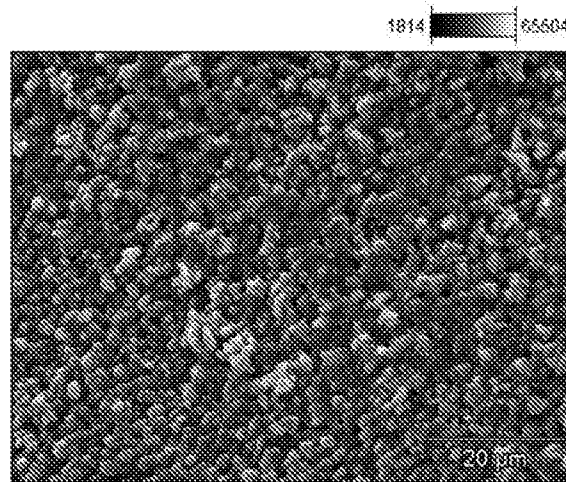


FIG. 5A

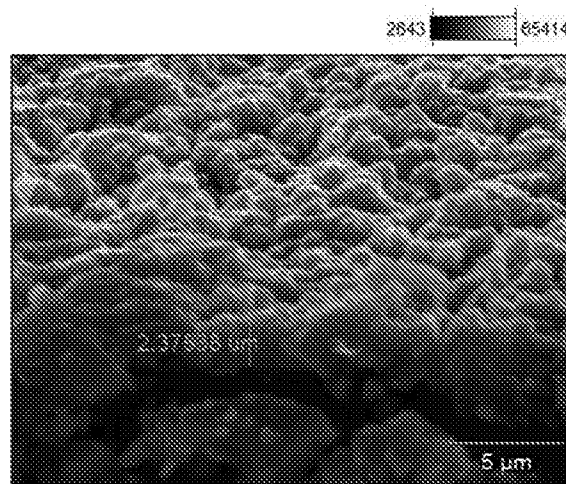


FIG. 5B

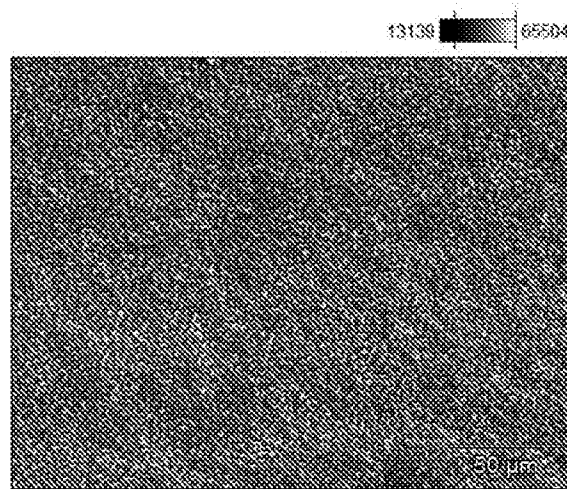


FIG. 6A

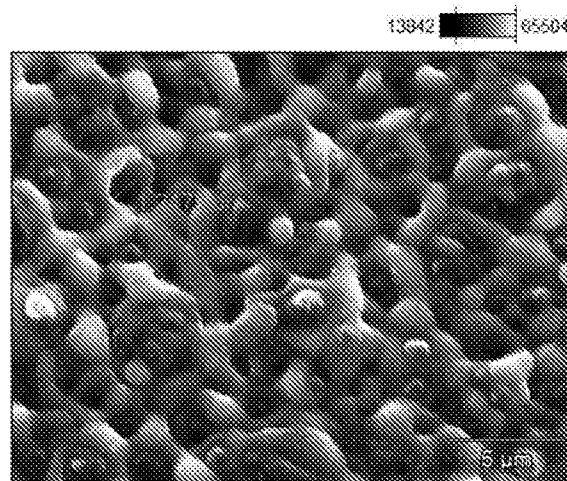


FIG. 6B

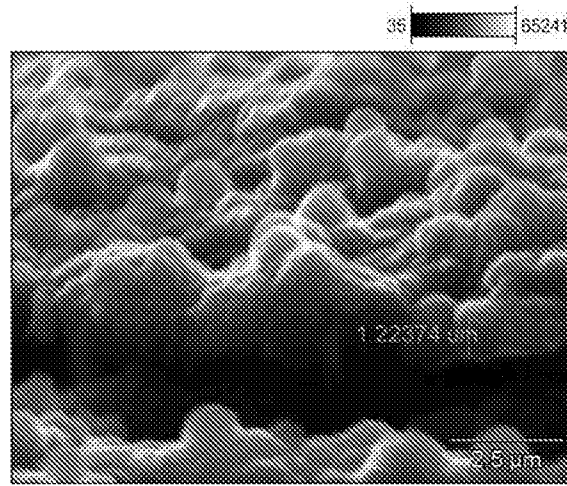


FIG. 6C

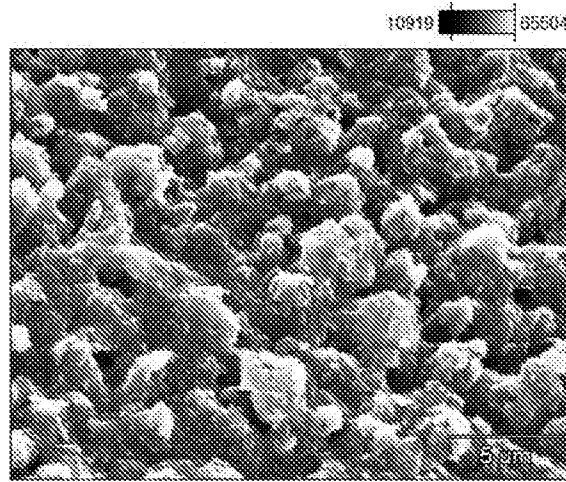


FIG. 7A

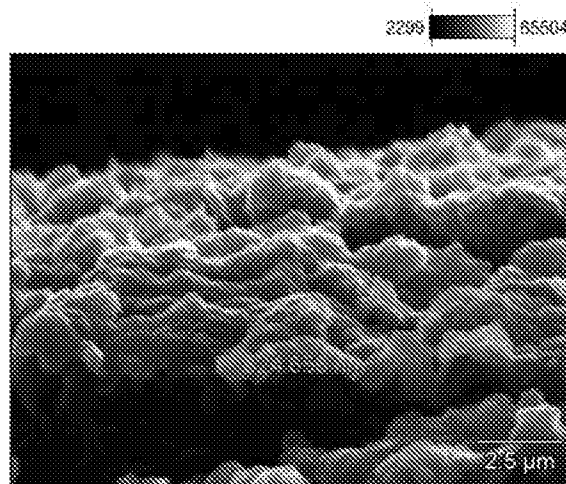


FIG. 7B

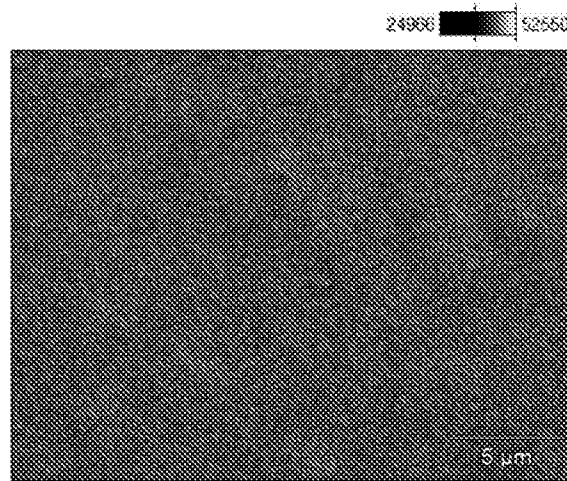


FIG. 8A

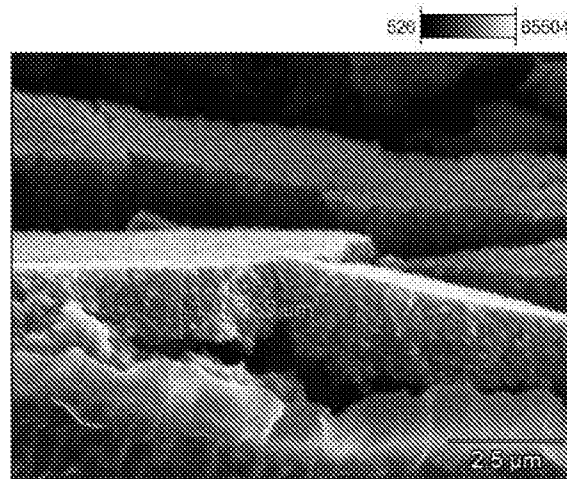


FIG. 8B

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2017/068181**A. CLASSIFICATION OF SUBJECT MATTER****H01M 4/134(2010.01)i, H01M 4/1395(2010.01)i, H01M 4/62(2006.01)i, H01M 4/38(2006.01)i, H01M 10/052(2010.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01M 4/134; H01M 2/16; H01M 4/583; H01M 10/0525; H01M 10/058; H01M 10/05; H01M 4/62; H01M 4/1395; H01M 4/38

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & keywords: protected electrode, alkali metal, lithium anode, alloy, alkali metal oxide, metal fluoride, carbon, graphite, intercalated ions

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2014-0220439 A1 (BADDING, MICHAEL EDWARD et al.) 07 August 2014 See claims 1-3, 5, 11, 13; and paragraphs [0006], [0011], [0022], [0024], [0053].	2,7
Y		1,3,4
Y	US 2015-0044517 A1 (SION POWER CORPORATION) 12 February 2015 See claims 1-3, 6, 8-10, 19; and paragraph [0060].	1
Y	KR 10-2014-0125970 A (UNIST ACADEMY-INDUSTRY RESEARCH CORPORATION) 30 October 2014 See claims 1, 2, 14; and paragraphs [0031], [0037], [0038], [0086]-[0089].	3,4
X	US 5387479 A (KOKSBANG, RENE) 07 February 1995 See claims 1-21; and column 2, line 22 - column 7, line 51.	5,6
A	US 2013-0309571 A1 (INDUSTRY-UNIVERSITY COOPERATION FOUNDATION HANYANG UNIVERSITY et al.) 21 November 2013 See claims 1-3, 7; and paragraphs [0079], [0085], [0143]-[0147], [0154], [0155].	5,6

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

23 April 2018 (23.04.2018)

Date of mailing of the international search report

23 April 2018 (23.04.2018)

Name and mailing address of the ISA/KR

International Application Division
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea

Facsimile No. +82-42-481-8578

Authorized officer

CHOI, Sang Won

Telephone No. +82-42-481-8291



Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: 12, 32, 37, 40, 41
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claims 12, 32, 37, 40 and 41 are substantially referring to the multiple dependent claims which do not comply with PCT Rule 6.4(a).

3. Claims Nos.: 8-11, 13-31, 33-36, 38, 39
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Group 1: claims 1-4, 7-23 and 25-41 are directed to: (i) a protected electrode structure comprising a composite protective structure comprising an alkali metal alloy; and (ii) a method of forming of a protected electrode comprising the step of forming a composite protective structure comprising an alkali metal alloy.

Group 2: claims 5, 6, 14, 20, 24-35 and 39-41 are directed to: (i) a protected electrode structure comprising a protective structure comprising elemental carbon and intercalated ions of an alkali metal; and (ii) a method of forming of a protected electrode comprising the step of forming a protective structure comprising an elemental carbon.

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.

3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2017/068181

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2014-0220439 A1	07/08/2014	CN 102881862 A CN 102881862 B EP 2732491 A1 IN 115DEN2014 A JP 2014-524120 A TW 201304254 A WO 2013-009429 A1	16/01/2013 25/03/2015 21/05/2014 22/05/2015 18/09/2014 16/01/2013 17/01/2013
US 2015-0044517 A1	12/02/2015	CN 105474448 A EP 3031096 A1 JP 2016-529671 A KR 10-2016-0040664 A WO 2015-021373 A1	06/04/2016 15/06/2016 23/09/2016 14/04/2016 12/02/2015
KR 10-2014-0125970 A	30/10/2014	None	
US 5387479 A	07/02/1995	None	
US 2013-0309571 A1	21/11/2013	CN 104541389 A EP 2850677 A1 EP 2850677 B1 JP 2015-520926 A KR 10-2013-0128273 A US 9391329 B2 WO 2013-172646 A1	22/04/2015 25/03/2015 04/10/2017 23/07/2015 26/11/2013 12/07/2016 21/11/2013