

ELECTROCHEMICAL METHOD OF FABRICATING AN ADHERENT AND STRUCTURALLY STABLE MULTILAYER ASSEMBLY

RELATED APPLICATION

[0001] The present patent document claims the benefit of priority under 35 U.S.C. 119(e) to U.S. Provisional Patent Application No. 63/617,210, which was filed on January 3, 2024, and is hereby incorporated by reference in its entirety.

FEDERALLY FUNDED RESEARCH OR DEVELOPMENT

[0002] This invention was made with government support under grant no. 1449548 awarded by the National Science Foundation. The government has certain rights in the invention.

TECHNICAL FIELD

[0003] The present disclosure is related generally to a method for improving adhesion in multilayer assemblies, and more particularly to an electrochemical method for preparing delamination-resistant oxide films for use in battery electrodes and other applications.

BACKGROUND

[0004] Lithium transition metal oxides, such as LiCoO_2 (LCO), are widely used as cathode materials for rechargeable lithium-ion batteries, which power electronic devices, electric vehicles, drones, power tools, medical devices, and other electronic components. Directly electrodeposited ceramic oxide (*e.g.*, LCO) film cathodes for alkali ion batteries could enable higher gravimetric and volumetric energy density electrodes due to the absence of binders and additives. The cathode materials may be integrated with a current collector, such as battery grade aluminum foil. Sufficient adhesion between the cathode material and the current collector is critical to ensure the mechanical integrity of the positive electrode during further processing and for successful functioning in a lithium-ion battery. Unfortunately, the electrodes may suffer from mechanical failure (decohesion) at the metal-metal oxide interface causing severe delamination, loss of electron-ion pathways and rapid degradation of the electrochemical performance. Mechanical failure is a major barrier to implementation of the electrodes in commercial lithium- or sodium-ion batteries. At present, there exists no general strategy for improving the adhesion quality and spallation life of electrochemically grown oxide films integrated to a current collector.

BRIEF DESCRIPTION OF THE DRAWINGS

[0005] FIG. 1A is a cross-sectional schematic of an exemplary adherent and structurally stable multilayer assembly, where the bonding layer is formed on the metallic interlayer due to passivation of only a surface region of the interlayer.

[0006] FIG. 1B is a cross-sectional schematic of an exemplary adherent and structurally stable multilayer assembly, where the bonding layer is formed on the base layer or substrate due to complete (through-thickness) passivation of the interlayer.

[0007] FIG. 2 is a cross-sectional schematic of an exemplary adherent and structurally stable multilayer assembly, where the base layer comprises a non-planar (curved) surface.

[0008] FIG. 3 is a cross-sectional schematic of an exemplary adherent and structurally stable multilayer assembly, where the base layer comprises a wire.

[0009] FIGS. 4A and 4B are cross-sectional schematics showing that adhesion between individual layers and mechanical integrity of the multilayer assembly may be independent of epitaxial relationships (or lack thereof) between individual layers. FIG. 4A shows a strong crystallographic orientation (epitaxial) relationship between the metallic interlayer and the base layer, and FIG. 4B shows no crystallographic orientation (epitaxial) relationship between the metallic interlayer and the base layer.

[0010] FIGS. 5A and 5B are cross-sectional schematics showing that adhesion between individual layers and mechanical integrity of the multilayer assembly may be independent of the texture of the top oxide overlayer.

[0011] FIG. 6A shows cyclic voltammetry curves obtained for a molten salt solution (including LiOH-KOH-Co(OH)₂) at 275°C ±5°C at sweep rates of 1 mV/s, 2 mV/s, 10 mV/s, and 100 mV/s, and associated scanning electron microscope (SEM) images from the multilayer assembly.

[0012] FIG. 6B shows cyclic voltammetry curves obtained for a molten salt solution (including LiOH-KOH-Co(OH)₂) at 300°C ±5°C at sweep rates of 1 mV/s, 2 mV/s, 10 mV/s, and 100 mV/s, and associated SEM images from the multilayer assembly.

[0013] FIG. 6C shows cyclic voltammetry curves obtained for a molten salt solution (including LiOH-KOH-Co(OH)₂) at 360°C ±5°C at sweep rates of 1 mV/s, 2 mV/s, 10 mV/s, and 100 mV/s, and associated SEM images from the multilayer assembly.

[0014] FIGS. 7A-7F show current profiles obtained from chronoamperometry experiments at various voltages (0.3 V, 0.4 V, 0.5 V, 0.6 V, 0.7 V, 0.8 V) for two different molten salt solution temperatures (300°C and 360°C); the profiles are labeled to indicate

whether passivation of the metallic interlayer occurs alone or in conjunction with growth of the top oxide layer.

[0015] FIG. 8 shows an SEM image and associated energy dispersive x-ray spectroscopy (EDS) elemental map of an adherent multilayer assembly formed from an aluminum base layer (50 μm), a nickel interlayer (2 μm) and an LCO top oxide layer (1000 μm).

[0016] FIG. 9 shows an SEM image and associated EDS elemental map of an adherent multilayer assembly formed from a stainless steel base layer (27 μm), a nickel interlayer (2 μm) and a LCO top oxide layer (60 μm).

[0017] FIG. 10 shows an SEM image and associated EDS elemental map of an adherent multilayer assembly formed from a carbon fiber woven paper base layer (5-10 μm), a nickel interlayer (1 μm) and an LCO top oxide layer (2 μm).

[0018] FIG. 11 shows an SEM image and associated EDS elemental map of an adherent multilayer assembly formed from a titanium base layer (27 μm), a nickel interlayer (2-10 μm) and an LCO top oxide layer (60 μm).

[0019] FIG. 12 shows an SEM image of an adherent multilayer assembly formed from a stainless steel base layer (27 μm), a nickel interlayer (2-10 μm) and an LMO top oxide layer (60 μm).

[0020] FIG. 13 shows an SEM image of an adherent multilayer assembly formed from an aluminum base layer (27 μm), a nickel interlayer (2-10 μm) and an LMO top oxide layer (20 μm).

[0021] FIG. 14 shows a cross-sectional schematic, SEM image, and EDS elemental map of an adherent multilayer assembly formed from a stainless steel base layer having a form factor of a wire (1 mm diameter), a nickel interlayer (2 μm) and an LCO top oxide layer (500 μm).

[0022] FIG. 15A is a schematic of an exemplary multilayer assembly being evaluated under pure tension and FIG. 15B shows associated adhesion failure strength results.

[0023] FIG. 16A is a schematic of an exemplary multilayer assembly being evaluated under pure shear and FIG. 16B shows associated adhesion failure strength results.

DETAILED DESCRIPTION

[0024] Described in this disclosure is an electrochemical solution-based method of fabricating an adherent and structurally stable multilayer assembly. The method may be used to form multilayer assemblies where adhesion of a metal oxide (“top oxide layer”) to a metallic base layer plays an important role in controlling the functional properties of the

assembly. Potential applications include oxide films bonded to a metallic substrate for electrochemical energy storage (*e.g.*, electrodes in Li ion and Na ion batteries), thermal barrier coatings, corrosion protection coatings, and/or oxide-based gas sensors integrated to a metallic substrate, where the quality of the interfacial adhesion may alter or affect ion-electron transfer, heat transfer, accelerated local chemical dissolution, and long-term structural stability at and across the metal-metal oxide interface. The electrochemical method and quality of adherence generated are demonstrated to be independent of the chemistry, type, thickness, dimensionality, epitaxial relationships and form factor of the base layer (substrate) and the top oxide layer.

[0025] The electrochemical method of fabricating an adherent multilayer assembly is described in general first and then in more detail below. The method includes forming a metallic interlayer on a substrate or base layer, electrochemically passivating some or all of the metallic interlayer such that a bonding layer comprising a binary oxide is formed, and then electrochemically growing a top oxide layer on the bonding layer. The bonding layer ensures strong adhesion of the top oxide layer and structural integrity of the multilayer assembly. In some examples, only a surface portion of the metallic interlayer undergoes electrochemical passivation, and the bonding layer is formed directly on the metallic interlayer, as illustrated in the cross-sectional schematic of FIG. 1A. In other examples, an entirety of the metallic interlayer undergoes electrochemical passivation, and the bonding layer is formed directly on the base layer or substrate, as illustrated in the cross-sectional schematic of FIG. 1B. Advantageously, the process conditions are controlled during electrochemical passivation such that the bonding layer is formed without pinholes or physical gaps. Accordingly, the bonding layer may provide complete areal coverage of the metallic interlayer and/or the base layer, thereby promoting or ensuring strong interfacial adhesion across the multilayer assembly. Experiments show that the interfacial adhesion strength of the multilayer assemblies described in this disclosure may be at least 100 times greater than that of conventional slurry cast electrodes. The inventors have discovered that strong adhesion may require complete areal coverage of the bonding layer and complete formation of the bonding layer prior to growth of the top oxide layer, as discussed below.

[0026] The metallic interlayer may comprise a metal capable of undergoing passivation to form the adherent binary oxide of the bonding layer. Suitable metals capable of forming thermally stable binary oxides include metals from groups 3-12, group 13 (Al, Ga, In, Tl, Nh); group 14 (Si, Ge, Sn, Pb, Fl); group 15 (As, Sb, Bi, Mc); and/or group 16 (Se, Te, Po, Lv). Particular examples may include nickel, aluminum, cobalt, manganese, iron and/or other

late transition metals. The metallic interlayer may be formed on the substrate by electroless deposition, electrochemical deposition, chemical vapor deposition, and/or physical vapor deposition (*e.g.*, e-beam evaporation or sputtering). The metallic interlayer may have a thickness in a range from 5 nm to 100 μm , or in some examples from 5 nm to 5 μm . The bonding layer formed upon passivation of the metallic interlayer typically has a thickness in a range from 5 nm to 10 μm , or from 5 nm to 1 μm . The bonding layer may comprise a binary oxide selected from the group consisting of aluminum oxide, nickel oxide, cobalt oxide, manganese oxide, and iron oxide. Also or alternatively, the binary oxide may be a transition metal oxide and/or may be formed from a group 13-16 metal (Al, Ga, In, Tl, Nh, Si, Ge, Sn, Pb, Fl, As, Sb, Bi, Mc, Se, Te, Po, and/or Lv). Advantageously, the binary oxide of the bonding layer has a thermal stability of 1000°C or higher, where the term “thermal stability” refers to resistance to degradation or melting.

[0027] The base layer or substrate may comprise a metallic and/or electrically conductive material such as a metal, an alloy, a conductive polymer, and/or a conductive composite. For battery electrode applications, the substrate may function as a current collector.

[0028] The top oxide formed on top of the bonding layer may comprise a ternary oxide. For battery electrode applications, the ternary oxide may comprise a cathode material, *e.g.*, an alkaline (Li, Na, K)/alkaline earth group (Ca, Mg) intercalated late transition group/group 13/low group 14-15 (Sn, Sb, Pb, Bi) oxide, individually, as a phase mixture, or as a doped version of the same. For example, the ternary oxide may include lithium or sodium in conjunction with a transition metal, such manganese or cobalt. Examples include lithium cobalt oxide, lithium manganese oxide, sodium cobalt oxide, and sodium manganese oxide. More specifically, the ternary metal oxide may comprise LiCoO_2 , NaCoO_2 , LiMnO_2 , or LiMn_2O_4 , $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$, and/or $\text{NaNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$, where $(x+y+z=1)$ and $0 \leq x, y, z \leq 1$. For applications other than energy storage, such as thermal barrier coatings, other ternary oxides, such as yttria-stabilized zirconia (YSZ) may be suitable. Typically, the top oxide layer has a thickness in a range from a 5 nm to 2000 μm , or from 5 μm to 1000 μm .

[0029] In one particular example of an adherent multilayer assembly, the top oxide layer may comprise a ternary metal oxide suitable for use as a lithium- or sodium-ion battery cathode material, such as LiCoO_2 , NaCoO_2 , LiMnO_2 , and/or LiMn_2O_4 , the bonding layer may comprise nickel oxide, the metallic interlayer may comprise nickel, and the substrate may comprise aluminum, stainless steel, titanium, and/or carbon.

[0030] In another particular example, the top oxide layer may comprise zirconia (ZrO_2) stabilized by yttria (Y_2O_3), that is, yttria-stabilized zirconia (YSZ), the bonding layer may comprise Al_2O_3 , the metallic interlayer may comprise a MCrAlY alloy, where M is Ni and/or Co, and the substrate may comprise a turbine blade alloy, such as a nickel-base superalloy.

[0031] To carry out the electrochemical passivation of some or all of the metallic interlayer, a working electrode and a counter electrode may be immersed in a non-aqueous bath comprising oxo (O^{2-}), hydroxo (OH^-), and/or peroxo (O_2^{2-}) radicals, where the working electrode is understood to include the base layer (substrate) and the metallic interlayer. The counter electrode may comprise an electrically conductive metal such as nickel or cobalt, or another transition metal. Preferably the counter electrode is electrochemically stable in the non-aqueous bath. In some examples, the counter electrode may take the form of a foil, sheet or foam. The non-aqueous bath may be described as a molten salt solution that includes an oxygen source. The molten salt solution may include a salt mixture, as discussed below. For battery electrode applications, the molten salt solution may also include a Li, Na, K, Cs, Rb, Ca, or Mg source and optionally a transition metal source. In some examples, the molten salt solution may include, in addition to the oxygen source, one or more transition metal sources.

[0032] A voltage above an oxidation potential for the metallic interlayer may be applied to the working electrode to effect passivation. The voltage may also be below a deposition potential for a transition metal component (*e.g.*, cobalt) of the top oxide layer to avoid simultaneous growth of the ternary oxide during passivation. The transition metal component may be a multivalent transition metal component for higher valent transitions (*e.g.*, +2 to +3, +2 to +4). In one example, the voltage is in a range from about 0.35 V to about 0.45 V vs. Co reference electrode to form the binary oxide. The applied voltage may be a constant voltage, and thus the application of the voltage may be described as a potentiostatic hold. In other examples, applying the voltage may comprise a galvanostatic, galvanodynamic, and/or potentiodynamic step. During the application of the voltage, the non-aqueous bath may be maintained at a temperature which is controlled as discussed below to ensure that electrochemical passivation of the metallic interlayer occurs prior to growth of the top oxide. Typically, the voltage is applied for a time period from 2-5 minutes to passivate the metallic interlayer and form the bonding layer comprising the binary oxide.

[0033] The oxo (O^{2-}), hydroxo (OH^-), and/or peroxo (O_2^{2-}) radicals in the non-aqueous bath or molten salt solution may be generated *in-situ* by electrochemical disintegration of a hydroxide (OH^-), halide (MX_n , X=F, Cl, Br, or I), nitrate (NO_3^-), nitrite (NO_2^-), sulfate (SO_4^{2-})

), sulfite (SO_3^{2-}), phosphate (PO_4^{3-}), phosphite (HPO_4^{2-}), acetate, carbonate, silicate or aluminate salt, or another suitable anion that may generate oxo/hydroxo/peroxo radicals. The molten salt solution may include, for example, LiOH , KOH , KNO_2 , KNO_3 , NaOH , Na_2O , NaNO_3 , NaNO_2 , Na_2SO_4 , CsOH , $\text{Ba}(\text{OH})_2$, K_2CO_3 , K_2SO_4 , LiNO_2 , LiNO_3 , Li_2CO_3 , LiCl , Li_2O_2 , Li_2SO_4 , and/or Li_2CO_3 . In some examples, the molten salt solution may include a salt mixture comprising LiOH-KOH , LiOH-NaOH , $\text{LiOH-NaOH-KOH-CsOH}$, NaOH-KOH , NaOH-CsOH , $\text{LiOH-Ba}(\text{OH})_2$, NaOH-KOH , $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$, $\text{LiNO}_3\text{-LiCl}$, or $\text{LiOH-Li}_2\text{CO}_3$. Alternatively, the salt mixture may comprise $\text{Li}_2\text{O-LiOH-KOH}$, $\text{Na}_2\text{O-NaOH-NaOH}$, $\text{Li}_2\text{O}_2\text{-LiOH-KOH}$, $\text{Li}_2\text{SO}_4\text{-Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$, $\text{LiNO}_3\text{-NaNO}_3\text{-KNO}_3$, or $\text{LiNO}_2\text{-NaNO}_2\text{-KNO}_2$.

[0034] Typically, the mixture of salts includes two or more hydroxides, such as lithium hydroxide and potassium hydroxide. A mass ratio of the lithium hydroxide to the potassium hydroxide may be in a range from about 0.5:8.5 to about 1.5:7.5, *e.g.*, about 1:8 (or 1.875:15). For formation of the bonding layer and the top oxide layer using the same non-aqueous bath, the mixture of salts may also include a transition metal source, such as cobalt hydroxide. In such an example, the mass ratio may be 1.875:15:1 (LiOH to KOH to $\text{Co}(\text{OH})_2$), or more generally speaking from the mass ratio of $\text{LiOH}:\text{KOH}$ may be from 1:2.67 to 1:16 and the mass ratio of $\text{KOH}:\text{Co}(\text{OH})_2$ may be up to 10:1. It may be advantageous to utilize a eutectic mixture of the salts, since the temperature required to melt the salts is decreased at the eutectic composition and thus the energy requirements of the process can be reduced. During electrochemical passivation/growth, the mixture of salts is heated at or above the melting temperature of the mixture, which in some examples may be in a range from 100°C to 800°C , but the temperature may be more tightly controlled (*e.g.*, $350\text{-}800^\circ\text{C}$, or $350\text{-}365^\circ\text{C}$) to ensure to complete electrochemical growth of the binary oxide (bonding layer) prior to growth of the ternary (top) oxide. Cyclic voltammetry experiments described below reveal that electrochemical passivation of the metallic interlayer at a temperature greater than 300°C (*e.g.*, at least 330°C , or at least 350°C) and a suitable voltage leads to complete (*e.g.*, pinhole-free) areal coverage of the binary oxide on the metallic interlayer/substrate without premature growth of the top oxide. In some examples, such as when chloride salt(s) are employed, oxygenation of the non-aqueous bath may be conducted by local controlled evolution or injection of O_2 gas (pure or as a mixture with an inert gas, Ar , N_2) near the working electrode.

[0035] Electrochemical passivation of the metallic interlayer to form the bonding layer and electrochemical growth of the top oxide layer may occur sequentially in the same non-aqueous bath, or in different non-aqueous baths. If electrochemical growth of the top oxide layer occurs in the same non-aqueous bath as passivation, then the voltage may be adjusted

(*e.g.*, increased) after passivation is completed to effect electrochemical growth of the ternary oxide on the bonding layer. For example, a LCO top oxide layer may begin to form at or above a voltage of 0.46 V vs. Co reference electrode using the same molten salt solution employed to form the bonding layer. For example, the voltage employed to grow the top oxide layer may be in the range from 0.46 V to 1.2 V vs. Co reference electrode.

Alternatively, a non-aqueous bath having a different chemistry (*e.g.*, further including a transition metal source) than the bath employed to form the bonding layer may be employed to grow the top oxide layer. In either case, electrochemical conditions known in the art to prepare the top oxide layer may be employed for electrodeposition. The method may further include an annealing step after electrochemical formation of the top oxide layer to crystallize the ternary oxide. In some examples, the annealing is carried out at an annealing temperature in a range from about 600°C to about 800°C. The adhesion strength is unaltered during annealing at these temperatures.

[0036] The method may involve electrochemical passivation and/or growth on planar or curved surfaces, as illustrated in the cross-sectional schematic of FIG. 2. In some examples, the substrate or base layer may have a form factor of a wire, on which a metallic interlayer (*e.g.*, Ni) may be conformally grown and then passivated to form the bonding layer (*e.g.*, NiO), followed by electrochemical growth of the top oxide layer (*e.g.*, LCO), as illustrated in the cross-sectional schematic of FIG. 3. Alternatively, the substrate or base layer may have the form factor of a foil on which the metallic interlayer, bonding layer and top oxide layer are formed. Generally speaking, the substrate or base layer may have any desired form factor (shape) and/or size. Experiments suggest that the radius of curvature of the individual layers (base layer, metallic bonding layer, top oxide layer) does not affect the interfacial adhesion provided by the bonding layer and/or the structural integrity of the multilayer assembly.

[0037] In fact, the interfacial adhesion provided by the bonding layer and the structural integrity of the multilayer assembly may be independent of the chemistry and physical characteristics of the multilayer assembly. For example, the interfacial adhesion and structural integrity may be independent of the materials selected for the base layer, the metallic interlayer, and the top oxide layer. The interfacial adhesion and structural integrity may also or alternatively be independent of the thickness and/or roughness of individual layers (base layer, metallic interlayer and top oxide layer) of the multilayer assembly. The interfacial adhesion and structural integrity may also or alternatively be independent of epitaxial relationships (or a lack thereof) between the base layer and the metallic interlayer, and/or between the metallic interlayer and the top oxide layer; *e.g.*, see the cross-sectional

schematic of FIG. 4A, where there is a strong orientation relationship between the metallic interlayer and the base layer or substrate, and the cross-sectional schematic of FIG. 4B, where there is no orientation relationship between the metallic interlayer and the base layer or substrate. As illustrated in FIGS. 5A and 5B, the interfacial adhesion provided by the bonding layer or the structural integrity of the multilayer assembly may not be affected by different textures of the top oxide layer.

[0038] Cyclic voltammetry and chronoamperometry experiments were carried out to explore the impact of temperature and voltage on the formation of an adherent bonding layer.

[0039] FIGS. 6A-6C show cyclic voltammetry curves and corresponding scanning electron microscope (SEM) images (magnification of 500x) of the electrodeposited samples after the cyclic voltammetry experiments, where “AG” indicates adherent growth and “NAG” indicates non-adherent growth. The cyclic voltammetry curves were obtained from a typical molten salt electroplating solution (in this example, a salt mixture comprising LiOH-KOH-Co(OH)₂) with a three electrode configuration (in this example, a Ni working electrode comprising nickel on stainless steel (or Al, Ti, or C foam), Ni counter electrode, cobalt reference electrode) under sweep rates of 1 mV/s (black), 2 mV/s (red), 10 mV/s (green), and 100 mV/s (violet) at 275°C (FIG. 6A), 300°C (FIG. 6B) and 360°C (FIG. 6C) $\pm 5^\circ\text{C}$.

[0040] At 275°C (FIG. 6A), only the (slow) sweep rate of 1 mV/s led to adherent growth of the bonding layer, and at 300°C (FIG. 6B), only the sweep rates of 1 mV/s and 2 mV/s led to adherent growth. In contrast, electrochemical passivation at a temperature of 360°C (FIG. 6C) led to adherent growth for all sweep rates (1 mV/s, 2 mV/s, 10 mV/s and even 100 mV/s). In the cyclic voltammetry curves, adherent growth can be discerned if the peak for a given sweep rate is distinct, as opposed to diffuse.

[0041] A key conclusion from the experimental findings is that, at elevated temperatures (*e.g.*, 360°C), nucleation and growth of electrodeposited material are significantly enhanced with a near complete thermodynamic takeover. In practice, this leads to extremely adherent electrodeposition at slow (1 mV/s) and extremely fast (100 mV/s) growth rates.

[0042] Chronoamperometry (observation of a current profile under a continuous voltage) experiments were conducted at different applied voltages (0.3 V, 0.4 V, 0.5 V, 0.6 V, 0.7 V, and 0.8 V vs. Co reference electrode (wire)) for two bath temperatures (300°C and 360°C) with a bath composition of LiOH, KOH and Co(OH)₂ with a mass ratio of 1.875:15:1. The resulting current profiles are shown in FIGS. 7A to 7F. The legends for individual experiments are written as [applied voltage]_[temperature in °C]_[mass of LiOH in g], *e.g.*

0.3_300_37.5. SEM images of top surface microstructure for the electrodeposited samples post-chronoamperometry are provided below the respective current profile.

[0043] A key conclusion from the experimental findings is that a potentiostatic hold at 0.4 V vs. Co wire solely leads to passivation (Ni to NiO oxidation). A potentiostatic hold higher than 0.4 V leads to concurrent passivation and electrocrystallization of LiCoO₂, which in turn affects the growth quality, desired microstructure, and subsequent electrochemical performance of the electrodeposit. A potentiostatic hold lower than 0.4 V leads to incomplete areal coverage of passivation. Passivation at an applied voltage of 0.4 V vs. Co reference electrode at 360 °C leads to complete areal passivation with desired strength. In the most preferred condition, the voltage window is 0.4 V (+/-0.05 V) for a duration of 2-4 mins at a temperature of 360 °C or higher.

EXAMPLES

[0044] Example 1. Adherent LiCoO₂ (top oxide layer) plating on planar aluminum (base layer)

[0045] A total of 400 g of KOH (reagent grade, ≥98%, anhydrous pellets) was dried in an Inconel crucible (250 mL capacity; Sigma) at 150 °C in a vacuum oven for 1 d and subsequently heated to 360 °C on a hotplate in a nitrogen or Ar-filled glovebox atmosphere (oxygen and water level <0.1 ppm), until the KOH solution was clear and dry. 25-125 g of LiOH (reagent grade, ≥98%, anhydrous pellets) was added to the crucible and the near eutectic mixture was allowed to equilibrate at 360 °C. 7.5-30 g of cobalt hydroxide was slowly added to the melt while stirring with a spatula. The solution was allowed to equilibrate for 8 hours post complete dissolution of the cobalt hydroxide.

[0046] A nickel (interlayer) coated aluminum foil (substrate/base layer) is used as the starting assembly for electrodeposition. The nickel was grown on aluminum foil by electroless deposition/electrochemical deposition/chemical vapor deposition/sputtering, or a successive combination of one or more of the abovementioned.

[0047] In the first step, the nickel coated aluminum is immersed in a bath temperature of 360°C (which is at least 350°C but not in excess of 365°C) with a bath composition of LiOH, KOH and Co(OH)₂ having a mass ratio of 1.875:15:1.

[0048] *Formation of the bonding layer:* In the next step, chronoamperometry (observation of a current profile under a continuous voltage) experiment is conducted at an applied voltage 0.4 V vs. Co wire at a bath temperature of 360°C with a bath composition of LiOH, KOH and Co(OH)₂ having a mass ratio of 1.875:15:1. A potentiostatic hold at 360°C

for 2-3 minutes creates a strong adhesion at the Ni-LCO (interlayer-top oxide layer) interface due to the formation of a bonding layer of NiO_x , as an interphase. It is noted that references to NiO_x in this disclosure may refer to stoichiometric nickel oxide (*e.g.*, NiO) or nonstoichiometric nickel oxide, where x may be, for example, slightly higher or lower than 1. This processing step is independent of the electrodeposition bath composition (LiOH-KOH-Co(OH)_2). Following this processing step, the assembly (base layer-interlayer-electrochemically formed bonding layer) is immersed in the desired electroplating solution for the final growth of LiCoO_2 .

[0049] *Composition of the non-aqueous bath:* The electrochemical formation of the stable bonding layer is caused by the formation of a passivating NiO_x layer completely covering the Ni surface without pinholes or physical gaps. The composition of the non-aqueous bath includes an oxo (O^{2-})/ hydroxo (OH^-)/ peroxy (O_2^{2-}) solvent as a single component/eutectic solution/a fraction of a non-eutectic solution. The oxo/hydroxo/peroxy radicals may be generated in-situ by electrochemical disintegration of nitrate NO_3^- , nitrite NO_2^- , sulfate (SO_4^{2-}), phosphate (PO_4^{3-}), phosphite (HPO_4^{2-}), or any similar anion that would generate oxo/hydroxo/peroxy radicals. The oxygenation of the non-aqueous solvent may be conducted by local controlled evolution of O_2 gas (pure or as a mixture with an inert gas, Ar, N_2) near the working electrode.

[0050] *Single pot vs. multipot synthesis:* The final electrochemical growth of LiCoO_2 may be conducted by any one of or combination of potentiostatic, potentiodynamic, galvanostatic, galvanodynamic, sweep rate in the same/different electroplating solution (one pot/multipot) at any desired temperature of choice. The adhesion of the multilayer assembly is established in the step of formation of the bonding layer.

[0051] The final multilayer assembly after electrodeposition of LCO top layer is demonstrated in FIG. 8. The thicknesses of the layers are base layer: aluminum ($50\text{ }\mu\text{m}$), metallic interlayer/bonding layer: nickel/ NiO_x : $2\text{ }\mu\text{m}$, top oxide layer: LCO: $\sim 1000\text{ }\mu\text{m}$. Scanning electron micrographs and overlaid EDS elemental maps elucidate the distinct multilayered structures, mechanical stability and continuity at the interfaces, elemental distributions (Al from base layer, Ni from metallic interlayer/bonding layer, and Co and O from LiCoO_2).

[0052] The typical thickness of the top oxide layer: a few nm to $2000\text{ }\mu\text{m}$ (*e.g.*, $5\text{ }\mu\text{m}$ to $1000\text{ }\mu\text{m}$). Examples include: LiCoO_2 ($2\text{ }\mu\text{m}$, $60\text{ }\mu\text{m}$, $500\text{ }\mu\text{m}$, $1000\text{ }\mu\text{m}$), LiMn_2O_4 ($20\text{ }\mu\text{m}$), and LiMnO_2 ($60\text{ }\mu\text{m}$).

[0053] The typical thickness of the base layer: a few nm to 2000 μm (*e.g.*, 5 μm to 1000 μm). Examples: stainless steel (27 μm flat foil, 1000 μm dia), Al (20 μm , 50 μm), C (10 μm), Ti (27 μm).

[0054] The typical thickness of the nickel interlayer/ NiO_x bonding layer: a few nm to 100 μm (*e.g.*, a few nm to 5 microns). Examples: nickel/nickel oxide (2 μm), manganese/manganese oxide (2 μm).

[0055] The typical thickness of the bonding layer formed by controlled electrochemical deposition: a few nm to 10 microns.

[0056] Example 2. Adherent LiCoO_2 (top oxide layer) plating on planar stainless steel (base layer)

[0057] Identical electrochemical process for formation of the bonding layer as Example 1, with a stainless-steel substrate.

[0058] Nickel was grown on stainless steel (SS) foil by electroless deposition/ electrochemical deposition/ chemical vapor deposition/sputtering, or a successive combination of one or more of the abovementioned.

[0059] The final multilayer assembly after electrodeposition of LCO top layer is demonstrated in FIG. 9. The thicknesses of the layers are base layer: SS (27 μm), metallic interlayer/bonding layer: nickel/ NiO_x : 2 μm , top oxide layer: LCO: $\sim 60 \mu\text{m}$. Scanning electron micrographs and overlaid EDS elemental maps elucidate the distinct multilayered structures, mechanical stability and continuity at the interfaces, elemental distributions (SS from base layer, Ni from interlayer/bonding layer, and Co and O from LiCoO_2).

[0060] Example 3. Adherent LiCoO_2 (top oxide layer) plating on porous carbon paper (base layer)

[0061] Identical electrochemical process for formation of the bonding layer as Example 1, with a substrate comprising 3D carbon paper / conductive carbon particles/ carbon nanotubes/ carbon fibers/ fullerenes/ graphene/ graphite/ pyrolytic carbon/ and/or glassy carbon.

[0062] Nickel was grown on a 3D carbon paper substrate by electroless deposition/ electrochemical deposition/ chemical vapor deposition/ sputtering, or a successive combination of the one or more of the abovementioned.

[0063] The final multilayer assembly after electrodeposition of LCO top layer is demonstrated in FIG. 10. The thicknesses of the layers are base layer: carbon (5-10 μm), metallic interlayer/bonding layer: nickel/ NiO_x : 1 μm , top oxide layer: LCO: $\sim 2 \mu\text{m}$.

Scanning electron micrographs and overlaid EDS elemental maps elucidate the distinct multilayered structures, mechanical stability and continuity at the interfaces, elemental distributions (C from base layer, Ni from interlayer/bonding layer, and Co and O from LiCoO_2).

[0064] Example 4. Adherent LiCoO_2 (top oxide layer) plating on titanium (base layer)

[0065] Identical electrochemical process for formation of the bonding layer as Example 1, with a titanium substrate. Identical LCO electroplating procedure for the top layer.

[0066] Nickel was grown on a Ti foil substrate by electroless deposition/ electrochemical deposition/ chemical vapor deposition/ sputtering, or a successive combination of one or more of the abovementioned.

[0067] The final multilayer assembly after electrodeposition of LCO top layer is demonstrated in FIG. 11. The thicknesses of the layers are base layer: Titanium ($27\text{ }\mu\text{m}$), metallic interlayer/bonding layer: nickel/ NiO_x : $2\text{-}10\text{ }\mu\text{m}$, top oxide layer: LCO: $\sim 60\text{ }\mu\text{m}$. Scanning electron micrographs and overlaid EDS elemental maps elucidate the distinct multilayered structures, mechanical stability and continuity at the interfaces, elemental distributions (Titanium from base layer, Ni from interlayer/bonding layer, and Co and O from LiCoO_2).

[0068] Example 5. Adherent LiMnO_2 (top oxide layer) plating on stainless steel (base layer)

[0069] A total of 400 g of KOH (reagent grade, $\geq 98\%$, anhydrous pellets) was dried in an Inconel crucible (250 mL capacity; Sigma) at $150\text{ }^\circ\text{C}$ in a vacuum oven for 1 d and subsequently heated to $360\text{ }^\circ\text{C}$ on a hotplate in a nitrogen or Ar-filled glovebox atmosphere (oxygen and water level $< 0.1\text{ ppm}$), until the KOH solution was clear and dry. 25-100 g of LiOH (reagent grade, $\geq 98\%$, anhydrous pellets) was added to the crucible and the near eutectic mixture was allowed to equilibrate at $360\text{ }^\circ\text{C}$. 10-50 g of manganese chloride was slowly added to the melt while stirring with a spatula. The solution was allowed to equilibrate for 8 hours post complete dissolution and complexation of the manganese chloride.

[0070] A nickel (metallic interlayer) coated stainless steel foil (substrate/base layer) is used as the starting assembly for electrodeposition. Nickel was grown on stainless steel foil by electroless deposition/ electrochemical deposition/ chemical vapor deposition/sputtering, or a successive combination of one or more of the abovementioned.

[0071] In the first step, the nickel coated stainless steel is immersed in a bath temperature of 360°C (which is at least 350°C but not in excess of 365°C) with a bath composition of LiOH, KOH and Mn(Cl)₂ having a mass ratio of 1.875:15:1.

[0072] *Formation of the bonding layer:* In the next step, an adherent bonding layer is grown for 3-5 minutes at 0.4 V vs. Co wire. The specific type/composition of the bath for the seed layer is not crucial to the adhesion. Normally, bath composition that will be same as the deposition step of the top oxide layer is chosen. A potentiostatic hold at 360°C for 2-3 minutes creates a strong adhesion at the Ni-LiMnO₂ (interlayer-top oxide layer) interface due to the formation of a bonding layer of NiO_x and MnO_x as an interphase. This processing step is independent of the electrodeposition bath composition (LiOH-KOH-Mn(Cl)₂). Following this processing step, the assembly (base layer-interlayer-electrochemically formed bonding layer) is immersed in the desired electroplating solution for the final growth of LiMnO₂.

[0073] *Single pot vs. multipot synthesis:* The final electrochemical growth of LiMnO₂ may be conducted by any one of or combinations of potentiostatic, potentiodynamic, galvanostatic, galvanodynamic, sweep rate in the same/different electroplating solution (one pot/multipot) at any desired temperature of choice. The adhesion of the multilayer assembly is established in the step of formation of the bonding layer.

[0074] The final multilayer assembly after electrodeposition of LiMnO₂ top layer is demonstrated in the SEM image of FIG. 12. The thicknesses of the layers are base layer: SS (27 μm), interlayer/bonding layer: nickel/NiO_x: 2-10 μm, top oxide layer: LiMnO₂: ~60 μm. Scanning electron micrographs and overlaid EDS elemental maps elucidate the distinct multilayered structures, mechanical stability and continuity at the interfaces, elemental distributions (Fe from base layer, Ni from interlayer/bonding layer, and Mn and O from LiMnO₂).

[0075] Example 6. Adherent LiMn₂O₄ (top oxide layer) plating on aluminum foil (base layer)

[0076] A total of 400 g of NaOH (reagent grade, ≥98%, anhydrous pellets) was dried in an Inconel crucible (250 mL capacity; Sigma) at 150 °C in a vacuum oven for 1 d and subsequently heated to 360 °C on a hotplate in a nitrogen or Ar-filled glovebox atmosphere (oxygen and water level <0.1 ppm), until the NaOH solution was clear and dry. 7.5-30 g of manganese chloride was slowly added to the melt while stirring with a spatula. The solution was allowed to equilibrate for 8 hours post complete dissolution and complexation of the MnCl₂/Mn₃O₄.

[0077] A nickel (interlayer) coated Al foil (substrate/base layer) is used as the starting assembly for electrodeposition. Nickel was grown on Al foil by electroless deposition/ electrochemical deposition/ chemical vapor deposition/sputtering, or a successive combination of one or more of the abovementioned.

[0078] In the first step, the nickel coated stainless steel is immersed in a bath temperature of 360°C (which is at least 350°C but not in excess of 365°C) with a bath composition of NaOH and $\text{Mn}(\text{Cl})_2$. In the next step, an adherent bonding layer is grown for 3-5 minutes at 0.4 V vs. Co wire. The specific type/composition of the bath for the seed layer is not crucial to the adhesion. Normally, bath composition that will be same as the deposition step of the top oxide layer is chosen.

[0079] *Formation of the bonding layer:* Chronoamperometry (observation of a current profile under a continuous voltage) experiment is conducted at an applied voltage 0.4 V vs. Co wire with a potentiostatic hold at 360°C for 2-3 minutes creating a strong adhesion at the Ni- NaMnO_2 (interlayer-top oxide layer) interface due to the formation of a bonding layer of NiO_x as an interphase. This processing step is independent of the electrodeposition bath composition (NaOH-MnCl_2). Following this processing step, the assembly (base layer-interlayer-electrochemically formed bonding layer) is immersed in the desired electroplating solution for the final growth of NaMnO_2 .

[0080] *Single pot vs. multipot synthesis:* The final electrochemical growth of NaMnO_2 may be conducted by any one of or combination of potentiostatic, potentiodynamic, galvanostatic, galvanodynamic, sweep rate in the same/different electroplating solution (one pot/multipot) at any desired temperature of choice. The adhesion of the multilayer assembly is established in the step of formation of the bonding layer.

[0081] Post deposition electroplated NaMnO_2 is immersed in a low melting eutectic ion exchange medium (LiCl-LiNO_3 1/5 w/w) at 450°C for 2 hours and further annealed at 600°C for 6 hours for converting NaMnO_2 to LiMn_2O_4 .

[0082] The final multilayer assembly after electrodeposition of the LiMn_2O_4 top layer is demonstrated in the SEM image of FIG. 13. The thicknesses of the layers are base layer: Aluminum (20 μm), interlayer/bonding layer: nickel/ NiO_x : 2 μm , top oxide layer: LiMn_2O_4 : ~20 μm . Scanning electron micrographs and overlayed EDS elemental maps elucidate the distinct multilayered structures, mechanical stability and continuity at the interfaces, elemental distributions (Al from base layer, Ni from interlayer/bonding layer, and Mn and O from LiMn_2O_4).

[0083] Example 7. Adherent LiCoO₂ (top oxide layer) plating on stainless steel wire (base layer)

[0084] A total of 400 g of KOH (reagent grade, ≥98%, anhydrous pellets) was dried in an Inconel crucible (250 mL capacity; Sigma) at 150 °C in a vacuum oven for 1 d and subsequently heated to 360 °C on a hotplate in a nitrogen or Ar-filled glovebox atmosphere (oxygen and water level <0.1 ppm), until the KOH solution was clear and dry. 25-100 g of LiOH (reagent grade, ≥98%, anhydrous pellets) was added to the crucible and the near eutectic mixture was allowed to equilibrate at 360 °C. 7.5-30 g of cobalt hydroxide was slowly added to the melt while stirring with a spatula. The solution was allowed to equilibrate for 8 hours post complete dissolution and complexation of the cobalt hydroxide.

[0085] A nickel (interlayer) coated stainless steel wire (substrate/base layer) is used as the starting assembly for electrodeposition. Nickel was grown on stainless steel foil by electroless deposition/ electrochemical deposition/ chemical vapor deposition/sputtering, or a successive combination of one or more of the abovementioned.

[0086] In the first step, the nickel coated stainless steel is immersed in a bath temperature of 360°C (which is at least 350°C but not in excess of 365°C) with a bath composition of LiOH, KOH and cobalt hydroxide having a mass ratio of 1.875:15:1. In the next step, an adherent bonding layer is grown for 3-5 minutes at 0.4 V vs. Co wire. The specific type/composition of the bath for the seed layer is not crucial to the adhesion. Normally, bath composition that will be same as the deposition step of the top oxide layer is chosen.

[0087] *Formation of the bonding layer:* Chronoamperometry (observation of a current profile under a continuous voltage) experiment was conducted at an applied voltage 0.4 V vs. Co wire at a bath temperature of 360°C with a bath composition of LiOH, KOH and Co(OH)₂ having a mass ratio of 1.875:15:1. A potentiostatic hold at 360°C for 2-3 minutes creates a strong adhesion at the Ni-LCO (interlayer-top oxide layer) interface due to the formation of a bonding layer of NiO_x as an interphase. This processing step is independent of the electrodeposition bath composition (LiOH-KOH-Co(OH)₂). Following this processing step, the assembly (base layer-interlayer-electrochemically formed bonding layer) is immersed in the desired electroplating solution for the final growth of LiCoO₂.

[0088] *Single pot vs. multipot synthesis:* The final electrochemical growth of LiCoO₂ may be conducted by any one of or combination of potentiostatic, potentiodynamic, galvanostatic, galvanodynamic, sweep rate in the same/different electroplating solution (one pot/multipot)

at any desired temperature of choice. The adhesion of the multilayer assembly is established in the step of formation of the bonding layer.

[0089] The final multilayer assembly after electrodeposition of LCO top layer is shown by the schematic, SEM image and EDS overlay of FIG. 14. The thicknesses of the layers are base layer: stainless steel: 1 mm diameter wire; interlayer/bonding layer: nickel/NiO_x: 2 μm, top oxide layer: LCO: ~500 μm. Scanning electron micrographs and overlaid EDS elemental maps elucidate the distinct multilayered structures, mechanical stability and continuity at the interfaces, elemental distributions (Fe from base layer, Ni from interlayer/bonding layer, and Co and O from LiCoO₂).

[0090] Example 8. Estimating adhesive failure strength in electrodeposited multilayer assemblies

[0091] The adhesive failure strength of electrodeposited multilayer assemblies including (1) stainless steel (base layer) 28 μm, nickel/nickel oxide (interlayer/bonding layer) ~250 nm, and LiCoO₂ (top oxide layer) 70 μm, (2) aluminum (base layer) 20 μm, nickel/nickel oxide (interlayer/bonding layer) ~250 nm, and LiCoO₂ (top oxide layer) 40 μm, and (3) stainless steel (base layer) 28 μm, nickel/nickel oxide (interlayer/bonding layer) ~250 nm, and LiCoO₂ (top oxide layer) 250 μm was evaluated and compared to that of slurry cast LCO prepared using conventional manufacturing methods.

[0092] Lower bounds for the adhesive failure strength in the multilayer assemblies were evaluated under pure tension (direct pull test), as illustrated in FIG. 15A. The lower tensile bound is at least ~10.4 MPa (FIG. 15B) for the multilayer assemblies with applications aimed at battery electrodes for lithium and sodium ion batteries. For conventional slurry cast material used in commercial battery cathode and anodes for lithium and sodium ion batteries, the adhesion strength is ~84.3 kPa. The adhesion strength for the multilayered assemblies produced by this method is at least 100 times greater than the interfacial adhesion strength of conventional slurry cast electrodes.

[0093] Lower bounds for the adhesive failure strength in the multilayer assemblies were evaluated under pure shear (interfacial shear test), as illustrated in FIG. 16A. The lower tensile bound is at least ~18.9 MPa (FIG. 16B) for the multilayer assemblies with applications aimed at battery electrodes for lithium and sodium ion batteries. For conventional slurry cast material used in commercial battery cathode and anodes for lithium and sodium ion batteries, the adhesion strength is ~3.27 MPa³.

[0094] The subject matter described in this disclosure may include the following aspects:

[0095] A first aspect relates to an electrochemical method of fabricating an adherent and structurally stable multilayer assembly, the method comprising: forming a metallic interlayer on a base layer; electrochemically passivating some or all of the metallic interlayer, thereby forming a bonding layer comprising a binary oxide; and electrochemically growing a top oxide layer on the bonding layer.

[0096] A second aspect relates to the electrochemical method of the first aspect, wherein only a surface portion of the metallic interlayer undergoes electrochemical passivation.

[0097] A third aspect relates to the electrochemical method of any preceding aspect, wherein an entirety of the metallic interlayer undergoes electrochemical passivation.

[0098] A fourth aspect relates to the electrochemical method of any preceding aspect, wherein the bonding layer is formed without pinholes or physical gaps, and/or wherein the bonding layer provides complete areal coverage of the metallic interlayer and/or the base layer.

[0099] A fifth aspect relates to the electrochemical method of any preceding aspect, wherein interfacial adhesion provided by the bonding layer and structural integrity of the multilayer assembly is independent of one or more chemical or physical characteristics of the multilayer assembly.

[00100] A sixth aspect relates to the electrochemical method of the preceding aspect, wherein the one or more chemical or physical characteristics are selected from the group consisting of materials employed for the base layer, the metallic interlayer, and the top oxide layer; thickness and/or roughness of the base layer, the metallic interlayer, and/or the top oxide layer; interfacial epitaxial relationships or a lack thereof between the base layer and the metallic interlayer, and/or between the metallic interlayer and the top oxide layer; and texture of the top oxide layer.

[00101] A seventh aspect relates to the electrochemical method of any preceding aspect, wherein the binary oxide is selected from the group consisting of aluminum oxide, nickel oxide, cobalt oxide, manganese oxide, and iron oxide, and/or the binary oxide comprises a transition metal oxide and/or includes a group 13-16 metal (Al, Ga, In, Tl, Nh, Si, Ge, Sn, Pb, Fl, As, Sb, Bi, Mc, Se, Te, Po, and/or Lv).

[00102] An eighth aspect relates to the electrochemical method of any preceding aspect, wherein the bonding layer has a thickness in a range from 5 nm to 10 μm , or from 5 nm to 1 μm .

- [00103] A ninth aspect relates to the electrochemical method of any preceding aspect, wherein the base layer comprises a metallic and/or electrically conductive material selected from the group consisting of a metal, an alloy, a conductive polymer, and a conductive composite.
- [00104] A tenth aspect relates to the electrochemical method of any preceding aspect, wherein the top oxide layer comprises a ternary oxide.
- [00105] An eleventh aspect relates to the electrochemical method of any preceding aspect, wherein the top oxide layer comprises an alkaline (Li, Na, K)/alkaline earth group (Ca, Mg) intercalated late transition group/group 13/low group 14-15 (Sn, Sb, Pb, Bi) oxide, individually, as a phase mixture, or as a doped version of the same.
- [00106] A twelfth aspect relates to the electrochemical method of any preceding aspect, wherein the top oxide layer comprises a ternary oxide selected from the group consisting of LiCoO_2 , NaCoO_2 , LiMnO_2 , LiMn_2O_4 , $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$, and $\text{NaNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$, where $(x+y+z=1)$ and $0 \leq x,y,z \leq 1$.
- [00107] A thirteenth aspect relates to the electrochemical method of any preceding aspect, wherein the top oxide layer has a thickness in a range from a 5 nm to 2000 μm , or from 5 μm to 1000 μm .
- [00108] A fourteenth aspect relates to the electrochemical method of any preceding aspect, wherein the metallic interlayer comprises a metal capable of forming the binary oxide, and wherein the binary oxide has a thermal stability of 1000°C or higher.
- [00109] A fifteenth aspect relates to the electrochemical method of any preceding aspect, wherein forming the metallic interlayer on the substrate comprises electroless deposition, electrochemical deposition, chemical vapor deposition, and/or physical vapor deposition.
- [00110] A sixteenth aspect relates to the electrochemical method of any preceding aspect, wherein the metallic interlayer has a thickness in a range from 5 nm to 100 μm , or from 5 nm to 5 μm .
- [00111] A seventeenth aspect relates to the electrochemical method of any preceding aspect, wherein electrochemically passivating some or all of the metallic interlayer comprises: immersing a working electrode and a counter electrode in a non-aqueous bath comprising oxo (O^{2-}), hydroxo (OH^-), and/or peroxo (O_2^{2-}) radicals, the working electrode comprising the base layer having the metallic interlayer thereon, the non-aqueous bath being at a temperature of at least 330°C; and applying a voltage above an oxidation potential of the metallic interlayer to the working electrode.

- [00112] An eighteenth aspect relates to the electrochemical method of the preceding aspect, wherein the temperature is in a range from 350°C to 365°C.
- [00113] A nineteenth aspect relates to the electrochemical method of any preceding aspect, wherein applying the voltage comprises a potentiostatic hold.
- [00114] A twentieth aspect relates to the electrochemical method of any preceding aspect, wherein applying the voltage includes a galvanostatic, galvanodynamic, and/or potentiodynamic step.
- [00115] A twenty-first aspect relates to the electrochemical method of any preceding aspect, wherein the voltage is below a deposition potential for a transition metal component of the top oxide layer, the transition metal component being a multivalent transition metal component for higher valent transitions (*e.g.*, +2 to +3, +2 to +4).
- [00116] A twenty-second aspect relates to the electrochemical method of any preceding aspect, wherein the voltage is in a range from about 0.35 V to about 0.45 V vs. Co reference electrode.
- [00117] A twenty-third aspect relates to the electrochemical method of any preceding aspect, wherein the non-aqueous bath comprises a molten salt solution including a Li, Na, K, Cs, Rb, Ca, or Mg source and optionally a transition metal source.
- [00118] A twenty-fourth aspect relates to the electrochemical method of any preceding aspect, the molten salt solution includes one or more salts selected from the group consisting of LiOH, KOH, KNO₂, KNO₃, NaOH, Na₂O, NaNO₃, NaNO₂, Na₂SO₄, CsOH, Ba(OH)₂, K₂CO₃, K₂SO₄, LiNO₂, LiNO₃, Li₂CO₃, LiCl, Li₂O₂, Li₂SO₄, and Li₂CO₃.
- [00119] A twenty-fifth aspect relates to the electrochemical method of any preceding aspect, wherein the molten salt solution includes a salt mixture selected from the group consisting of LiOH-KOH, LiOH-NaOH, LiOH-NaOH-KOH-CsOH, NaOH-KOH, NaOH-CsOH, LiOH-Ba(OH)₂, NaOH-KOH, Li₂CO₃-K₂CO₃, LiNO₃-LiCl, and LiOH-Li₂CO₃.
- [00120] A twenty-sixth aspect relates to the electrochemical method of any preceding aspect, wherein the molten salt solution includes a salt mixture selected from the group consisting of Li₂O-LiOH-KOH, Na₂O-NaOH-NaOH, Li₂O₂-LiOH-KOH, Li₂SO₄-Na₂SO₄-K₂SO₄, LiNO₃-NaNO₃-KNO₃, and LiNO₂-NaNO₂-KNO₂.
- [00121] A twenty-seventh aspect relates to the electrochemical method of any preceding aspect, wherein the oxo (O²⁻), hydroxo (OH⁻), and/or peroxo (O₂²⁻) radicals are generated *in situ* by electrochemical disintegration of a hydroxide (OH⁻), halide (MX_n, X=F, Cl, Br, or I),

nitrate (NO_3^-), nitrite (NO_2^-), sulfate (SO_4^{2-}), sulfite (SO_3^{2-}), phosphate (PO_4^{3-}), phosphite (HPO_4^{2-}), acetate, carbonate, silicate, aluminate, or another anion.

[00122] A twenty-eighth aspect relates to the electrochemical method of any preceding aspect, further comprising oxygenation of the non-aqueous bath by controlled evolution or injection of a gas comprising O_2 near the working electrode.

[00123] A twenty-ninth aspect relates to the electrochemical method of any preceding aspect, further comprising an annealing treatment to crystallize the top oxide layer.

[00124] A thirtieth aspect relates to the electrochemical method of any preceding aspect, wherein the top oxide layer comprises LiCoO_2 , NaCoO_2 , LiMnO_2 , and/or LiMn_2O_4 ; the bonding layer comprises nickel oxide; the metallic interlayer comprises nickel; and the base layer comprises aluminum, stainless steel, titanium, and/or carbon.

[00125] A thirty-second aspect relates to the electrochemical method of any preceding aspect, wherein the top oxide layer comprises zirconia (ZrO_2) stabilized by yttria (Y_2O_3); the bonding layer comprises Al_2O_3 ; the metallic interlayer comprises a MCrAlY alloy, where M is Ni and/or Co; and the base layer comprises a turbine blade alloy.

[00126] A thirty-third aspect relates to the electrochemical method of any preceding aspect, wherein the base layer comprises a planar surface.

[00127] A thirty-fourth aspect relates to the electrochemical method of any preceding aspect, wherein the base layer comprises a curved surface.

[00128] A thirty-fifth aspect relates to the electrochemical method of any preceding aspect, wherein the base layer has a form factor of a wire.

[00129] A thirty-sixth aspect relates to an adherent and structurally stable multilayer assembly comprising: a bonding layer comprising a binary oxide on a base layer; and a top oxide layer on the bonding layer, the top oxide layer comprising a ternary oxide.

[00130] A thirty-seventh aspect relates to the multilayer assembly of the preceding aspect, wherein the bonding layer is formed by electrochemical passivation of a metallic interlayer on the base layer.

[00131] A thirty-eighth aspect relates to the multilayer assembly of any preceding aspect, wherein the bonding layer is devoid of pinholes or physical gaps, and/or wherein the bonding layer provides complete areal coverage of the metallic interlayer and/or the base layer.

[00132] A thirty-ninth aspect relates to the multilayer assembly of any preceding aspect, wherein the binary oxide is selected from the group consisting of aluminum oxide, nickel oxide, cobalt oxide, manganese oxide, and iron oxide, and/or wherein the binary oxide

comprises a transition metal oxide and/or comprises a group 13-16 metal (Al, Ga, In, Tl, Nh, Si, Ge, Sn, Pb, Fl, As, Sb, Bi, Mc, Se, Te, Po, and/or Lv).

[00133] A fortieth aspect relates to the multilayer assembly of any preceding aspect, wherein the bonding layer has a thickness in a range from 5 nm to 10 μm , or from 5 nm to 1 μm .

[00134] A forty-first aspect relates to the multilayer assembly of any preceding aspect, wherein the base layer comprises a metallic and/or an electrically conductive material selected from the group consisting of a metal, an alloy, a conductive polymer, and a conductive composite.

[00135] A forty-second aspect relates to the multilayer assembly of any preceding aspect, wherein the top oxide layer comprises a ternary oxide.

[00136] A forty-third aspect relates to the multilayer assembly of any preceding aspect, wherein the top oxide layer comprises an alkaline (Li, Na, K)/alkaline earth group (Ca, Mg) intercalated late transition group/group 13/low group 14-15 (Sn, Sb, Pb, Bi) oxide, individually, as a phase mixture, or as a doped version of the same.

[00137] A forty-fourth aspect relates to the multilayer assembly of any preceding aspect, wherein the top oxide layer comprises ternary oxide selected from the group consisting of LiCoO_2 , NaCoO_2 , LiMnO_2 , LiMn_2O_4 , $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$, and $\text{NaNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$, where $(x+y+z=1)$ and $0 \leq x, y, z \leq 1$.

[00138] A forty-fifth aspect relates to the multilayer assembly of any preceding aspect, wherein the top oxide layer has a thickness in a range from a 5 nm to 2000 μm , or from 5 μm to 1000 μm .

[00139] A forty-sixth aspect relates to the multilayer assembly of any preceding aspect, wherein the top oxide layer comprises LiCoO_2 , NaCoO_2 , LiMnO_2 , and/or LiMn_2O_4 ; the bonding layer comprises nickel oxide; and the base layer comprises aluminum, stainless steel, titanium, and/or carbon.

[00140] A forty-seventh aspect relates to the multilayer assembly of any preceding aspect, wherein the top oxide layer comprises zirconia (ZrO_2) stabilized by yttria (Y_2O_3); the bonding layer comprises Al_2O_3 ; and the base layer comprises a turbine blade alloy.

[00141] A forty-eighth aspect relates to the multilayer assembly of any preceding aspect, wherein the base layer comprises a planar surface.

[00142] A forty-ninth aspect relates to the multilayer assembly of any preceding aspect, wherein the base layer comprises a curved surface.

[00143] A fiftieth aspect relates to the multilayer assembly of any preceding aspect, wherein the base layer has a form factor of a wire.

[00144] A fifty-first aspect relates to the multilayer assembly of any preceding aspect, wherein the top oxide layer comprises a cathode material and the base layer comprises a current collector for a lithium- or sodium-ion battery.

[00145] A fifty-second aspect relates to the multilayer assembly of any preceding aspect, wherein the top oxide layer comprises a thermal barrier coating, a corrosion protection coating, and/or an oxide-based gas sensor, and wherein the base layer comprises a metallic substrate.

[00146] Although the present invention has been described in considerable detail with reference to certain embodiments thereof, other embodiments are possible without departing from the present invention. The spirit and scope of the appended claims should not be limited, therefore, to the description of the preferred embodiments contained herein. All embodiments that come within the meaning of the claims, either literally or by equivalence, are intended to be embraced therein.

[00147] Furthermore, the advantages described above are not necessarily the only advantages of the invention, and it is not necessarily expected that all of the described advantages will be achieved with every embodiment of the invention.

CLAIMS

1. An electrochemical method of fabricating an adherent and structurally stable multilayer assembly, the method comprising:
 - forming a metallic interlayer on a base layer;
 - electrochemically passivating some or all of the metallic interlayer, thereby forming a bonding layer comprising a binary oxide; and
 - electrochemically growing a top oxide layer on the bonding layer.
2. The electrochemical method of claim 1, wherein only a surface portion of the metallic interlayer undergoes electrochemical passivation.
3. The electrochemical method of claim 1, wherein an entirety of the metallic interlayer undergoes electrochemical passivation.
4. The electrochemical method of claim 1, wherein the bonding layer is formed without pinholes or physical gaps, and/or
 - wherein the bonding layer provides complete areal coverage of the metallic interlayer and/or the base layer.
5. The electrochemical method of claim 1, wherein interfacial adhesion provided by the bonding layer and structural integrity of the multilayer assembly is independent of one or more chemical or physical characteristics of the multilayer assembly.
6. The electrochemical method of claim 5, wherein the one or more chemical or physical characteristics are selected from the group consisting of:
 - materials employed for the base layer, the metallic interlayer, and the top oxide layer;
 - thickness and/or roughness of the base layer, the metallic interlayer, and/or the top oxide layer;
 - interfacial epitaxial relationships or a lack thereof between the base layer and the metallic interlayer, and/or between the metallic interlayer and the top oxide layer; and
 - texture of the top oxide layer.

7. The electrochemical method of claim 1, wherein the binary oxide is selected from the group consisting of aluminum oxide, nickel oxide, cobalt oxide, manganese oxide, and iron oxide, and/or
the binary oxide is a transition metal oxide and/or is formed from a group 13-16 metal (Al, Ga, In, Tl, Nh, Si, Ge, Sn, Pb, Fl, As, Sb, Bi, Mc, Se, Te, Po, and/or Lv).
8. The electrochemical method of claim 1, wherein the bonding layer has a thickness in a range from 5 nm to 10 μm , or from 5 nm to 1 μm .
9. The electrochemical method of claim 1, wherein the base layer comprises a metallic and/or electrically conductive material selected from the group consisting of a metal, an alloy, a conductive polymer, and a conductive composite.
10. The electrochemical method of claim 1, wherein the top oxide layer comprises a ternary oxide.
11. The electrochemical method of claim 1, wherein the top oxide layer comprises an alkaline (Li, Na, K)/alkaline earth group (Ca, Mg) intercalated late transition group/group 13/low group 14-15 (Sn, Sb, Pb, Bi) oxide, individually, as a phase mixture, or as a doped version of the same.
12. The electrochemical method of claim 1, wherein the top oxide layer comprises a ternary oxide selected from the group consisting of LiCoO_2 , NaCoO_2 , LiMnO_2 , LiMn_2O_4 , $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$, and $\text{NaNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$, where $(x+y+z=1)$ and $0 \leq x, y, z \leq 1$.
13. The electrochemical method of claim 1, wherein the top oxide layer has a thickness in a range from a 5 nm to 2000 μm , or from 5 μm to 1000 μm .
14. The electrochemical method of claim 1, wherein the metallic interlayer comprises a metal capable of forming the binary oxide, and
wherein the binary oxide has a thermal stability of 1000°C or higher.

15. The electrochemical method of claim 1, wherein forming the metallic interlayer on the substrate comprises electroless deposition, electrochemical deposition, chemical vapor deposition, and/or physical vapor deposition.
16. The electrochemical method of claim 1, wherein the metallic interlayer has a thickness in a range from 5 nm to 100 μm , or from 5 nm to 5 μm .
17. The electrochemical method of claim 1, wherein electrochemically passivating some or all of the metallic interlayer comprises:
immersing a working electrode and a counter electrode in a non-aqueous bath comprising oxo (O^{2-}), hydroxo (OH^-), and/or peroxo (O_2^{2-}) radicals, the working electrode comprising the base layer having the metallic interlayer thereon, the non-aqueous bath being at a temperature of at least 330°C; and
applying a voltage above an oxidation potential of the metallic interlayer to the working electrode.
18. The electrochemical method of claim 17, wherein the temperature is in a range from 350°C to 365°C.
19. The electrochemical method of claim 17, wherein applying the voltage comprises a potentiostatic hold.
20. The electrochemical method of claim 17, wherein applying the voltage includes a galvanostatic, galvanodynamic, and/or potentiodynamic step.
21. The electrochemical method of claim 17, wherein the voltage is below a deposition potential for a transition metal component of the top oxide layer.
22. The electrochemical method of claim 17, wherein the voltage is in a range from about 0.35 V to about 0.45 V vs. Co reference electrode.
23. The electrochemical method of claim 17, wherein the non-aqueous bath comprises a molten salt solution including a Li, Na, K, Cs, Rb, Ca, or Mg source and optionally a transition metal source.

24. The electrochemical method of claim 23, wherein the molten salt solution includes one or more salts selected from the group consisting of LiOH, KOH, KNO₂, KNO₃, NaOH, Na₂O, NaNO₃, NaNO₂, Na₂SO₄, CsOH, Ba(OH)₂, K₂CO₃, K₂SO₄, LiNO₂, LiNO₃, Li₂CO₃, LiCl, Li₂O₂, Li₂SO₄, and Li₂CO₃.

25. The electrochemical method of claim 23, wherein the molten salt solution includes a salt mixture selected from the group consisting of LiOH-KOH, LiOH-NaOH, LiOH-NaOH-KOH-CsOH, NaOH-KOH, NaOH-CsOH, LiOH-Ba(OH)₂, NaOH-KOH, Li₂CO₃-K₂CO₃, LiNO₃-LiCl, and LiOH-Li₂CO₃.

26. The electrochemical method of claim 23, wherein the molten salt solution includes a salt mixture selected from the group consisting of Li₂O-LiOH-KOH, Na₂O-NaOH-NaOH, Li₂O₂-LiOH-KOH, Li₂SO₄-Na₂SO₄-K₂SO₄, LiNO₃-NaNO₃-KNO₃, and LiNO₂-NaNO₂-KNO₂.

27. The electrochemical method of claim 17, wherein the oxo (O²⁻), hydroxo (OH⁻), and/or peroxo (O₂²⁻) radicals are generated *in situ* by electrochemical disintegration of a hydroxide (OH⁻), halide (MX_n, X=F, Cl, Br, or I), nitrate (NO₃⁻), nitrite (NO₂⁻), sulfate (SO₄²⁻), sulfite (SO₃²⁻), phosphate (PO₄³⁻), phosphite (HPO₄²⁻), acetate, carbonate, silicate, aluminate, or another anion.

28. The electrochemical method of claim 17, further comprising oxygenation of the non-aqueous bath by controlled evolution or injection of a gas comprising O₂ near the working electrode.

29. The electrochemical method of claim 1, further comprising an annealing treatment to crystallize the top oxide layer.

30. The electrochemical method of claim 1, wherein the top oxide layer comprises LiCoO₂, NaCoO₂, LiMnO₂, and/or LiMn₂O₄;
the bonding layer comprises nickel oxide;
the metallic interlayer comprises nickel; and

the base layer comprises aluminum, stainless steel, titanium, and/or carbon.

31. The electrochemical method of claim 1, wherein the top oxide layer comprises zirconia (ZrO_2) stabilized by yttria (Y_2O_3);
the bonding layer comprises Al_2O_3 ;
the metallic interlayer comprises a MCrAlY alloy, where M is Ni and/or Co; and
the base layer comprises a turbine blade alloy.

32. The electrochemical method of claim 1, wherein the base layer comprises a planar surface.

33. The electrochemical method of claim 1, wherein the base layer comprises a curved surface.

34. The electrochemical method of claim 1, wherein the base layer has a form factor of a wire.

35. An adherent and structurally stable multilayer assembly comprising:
a bonding layer comprising a binary oxide on a base layer; and
a top oxide layer on the bonding layer, the top oxide layer comprising a ternary oxide.

36. The adherent and structurally stable multilayer assembly of claim 35, wherein the bonding layer is formed by electrochemical passivation of a metallic interlayer on the base layer.

37. The adherent and structurally stable multilayer assembly of claim 35, wherein the bonding layer is devoid of pinholes or physical gaps, and/or
wherein the bonding layer provides complete areal coverage of the metallic interlayer and/or the base layer.

38. The adherent and structurally stable multilayer assembly of claim 35, wherein the binary oxide is selected from the group consisting of aluminum oxide, nickel oxide, cobalt oxide, manganese oxide, and iron oxide, and/or

wherein the binary oxide is a transition metal oxide and/or is formed from a group 13-16 metal (Al, Ga, In, Tl, Nh, Si, Ge, Sn, Pb, Fl, As, Sb, Bi, Mc, Se, Te, Po, and/or Lv).

39. The adherent and structurally stable multilayer assembly of claim 35, wherein the bonding layer has a thickness in a range from 5 nm to 10 μm , or from 5 nm to 1 μm .

40. The adherent and structurally stable multilayer assembly of claim 35, wherein the base layer comprises a metallic and/or an electrically conductive material selected from the group consisting of a metal, an alloy, a conductive polymer, and a conductive composite.

41. The adherent and structurally stable multilayer assembly of claim 35, wherein the top oxide layer comprises a ternary oxide.

42. The adherent and structurally stable multilayer assembly of claim 35, wherein the top oxide layer comprises an alkaline (Li, Na, K)/alkaline earth group (Ca, Mg) intercalated late transition group/group 13/low group 14-15 (Sn, Sb, Pb, Bi) oxide, individually, as a phase mixture, or as a doped version of the same.

43. The adherent and structurally stable multilayer assembly of claim 35, wherein the top oxide layer comprises a ternary oxide selected from the group consisting of LiCoO_2 , NaCoO_2 , LiMnO_2 , LiMn_2O_4 , $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$, and $\text{NaNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$, where $(x+y+z=1)$ and $0 \leq x, y, z \leq 1$.

44. The adherent and structurally stable multilayer assembly of claim 35, wherein the top oxide layer has a thickness in a range from a 5 nm to 2000 μm , or from 5 μm to 1000 μm .

45. The adherent and structurally stable multilayer assembly of claim 35, wherein the top oxide layer comprises LiCoO_2 , NaCoO_2 , LiMnO_2 , and/or LiMn_2O_4 ;
the bonding layer comprises nickel oxide; and
the base layer comprises aluminum, stainless steel, titanium, and/or carbon.

46. The adherent and structurally stable multilayer assembly of claim 35, wherein the top oxide layer comprises zirconia (ZrO_2) stabilized by yttria (Y_2O_3);

the bonding layer comprises Al_2O_3 ; and
the base layer comprises a turbine blade alloy.

47. The adherent and structurally stable multilayer assembly of claim 35, wherein the base layer comprises a planar surface.

48. The adherent and structurally stable multilayer assembly of claim 35, wherein the base layer comprises a curved surface.

49. The adherent and structurally stable multilayer assembly of claim 35, wherein the base layer has a form factor of a wire.

50. The adherent and structurally stable multilayer assembly of claim 35, wherein the top oxide layer comprises a cathode material and the base layer comprises a current collector for a lithium- or sodium-ion battery.

51. The adherent and structurally stable multilayer assembly of claim 35, wherein the top oxide layer comprises a thermal barrier coating, a corrosion protection coating, and/or an oxide-based gas sensor, and wherein the base layer comprises a metallic substrate.