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(54) Title: POSITIVE ELECTRODES FOR RECHARGEABLE BATTERIES

(57) Abstract: Disclosed herein is a cathode electrode for a reversible battery comprising an active material comprising an alkali metal ion or alkaline-earth metal ion and at least one or more transition metal chalcogenides, and wherein active redox species comprise anions. Also disclosed are secondary batteries comprising such cathode electrodes. Also disclosed are methods of making the disclosed herein cathode electrodes and secondary batteries.

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POSITIVE ELECTRODES FOR RECHARGEABLE BATTERIES

CROSS-REFERENCE TO RELATED APPLICATIONS

[001] This application claims the benefit of priority to Chinese Application No. 202310523783.0, filed on May 11, 2023, and the benefit of U.S. Provisional Application No.63/564,029, filed March 12, 2024, the contents of which are incorporated herein by reference in their entirety.

STATEMENT ACKNOWLEDGING GOVERNMENT SUPPORT

[002] This invention was made with government support under Grant No. DE-SC0005397 awarded by the Department of Energy. The government has certain rights in the invention.

TECHNICAL FIELD

[003] This application relates generally to positive electrodes in rechargeable batteries.

BACKGROUND

[004] It is one of the global strategies to avoid the energy crisis and environmental degradation by developing renewable, clean energy; rechargeable batteries are the core of renewable energy technologies and are broad in application, such as electric vehicles, large-scale energy storage systems, and some emerging applications requiring high-energy-density (such as electric aircraft and trucks). Lithium-ion batteries have always been dominant in the battery market with their characteristics of relatively high energy ratio, long service life, high-power tolerance, light weight, green and environmental protection, etc. However, the global demand for rechargeable batteries with high energy density has increased significantly, and thus, over-reliance on lithium-ion batteries is unrealistic due to high prices and scarcity of resources. To this end, it is necessary to turn to the exploration of novel battery systems to meet the enormous demand in the future.

[005] For example, sodium-ion batteries (SIBs) or potassium-ion batteries are an exciting post-lithium energy storage alternative. In addition to abundant sodium resources and low cost, they also have a "rocking chair" mechanism similar to lithium-ion batteries, and the sodium-ion batteries (and potentially potassium-ion

batteries) are recognized as ideal secondary batteries suitable for future low-speed electric vehicles and large-scale energy storage systems, etc.

[006] However, existing sodium-ion battery positive electrode materials have many problems: low sodium storage capacity, poor long-term cycle stability and high-rate characteristics, high preparation costs, etc. It is one of the keys to the practical application of sodium-ion energy storage batteries to find low-cost sodium-ion battery positive electrode materials with excellent sodium storage performance.

[007] Traditional sodium-ion battery positive electrode materials comprise, for example, layered transition metal oxides Na_xMO_2 (M is Mn, Fe, Co, Ni) and Mn, Fe cyanide or manganese- and iron-based coordinated Prussian blue or white compounds, polyanionic vanadium-based phosphates or pyrophosphates, etc. The positive electrode materials are charged and discharged based on a deintercalation reaction, resulting in an unstable structure of the materials in the charging and discharging process, which is prone to generate irreversible phase transitions and leads to low practical capacity.

[008] On the other hand, for a novel sodium-sulfur battery system, there is an intermediate product, sodium polysulfide, which is easily dissolved in the electrolyte, causing a "shuttle effect" to occur, causing active substances to lose, thereby resulting in a short cycle life.

[009] Thus, novel and suitable positive electrode materials with fast diffusion kinetics, excellent rate performance, and high energy density are needed. These needs and other needs are at least partially satisfied by the present disclosure.

SUMMARY

[010] The present disclosure is directed to a cathode electrode for a reversible battery comprising an active material comprising an alkali metal ion or alkaline-earth metal ion and at least one or more transition metal chalcogenides, and wherein active redox species comprise anions.

[011] In still further aspects, the active material is represented by $\text{M}^1\text{M}^2\text{X}$, wherein M^1 comprises Li, Na, K, or a combination thereof; wherein M^2 comprises at least one transition metal ion comprising Co, Fe, Mn, Ni, V, Ti, Cr, Cu, Zr, Nb, Ta, Mo, W, Pd, Pt, Re, Cd, or a combination thereof; wherein X comprises S, Se, Te, O, or a

combination thereof; and wherein M^1 , M^2 , and X are present in a predetermined ratio.

[012] In yet still further aspects, the active material further comprises Y and is represented by M^1M^2XY , wherein Y comprises a halogen, and wherein M^1 , M^2 , X, and Y are present in a predetermined ratio.

[013] In yet still further aspects, the active material is represented by $M_a^1M_b^2X_cY_d$, wherein M^1 is Na, $2 \leq a \leq 7$, M^2 is one of Co, Fe, Mn, Ni, V, Ti, Cr, Cu, Zr, Nb, Ta, Mo, W, Pd, Pt, Re, Cd, or a combination thereof, wherein $0 < b \leq 2$; X is one or more of S, Se, Te, O, or a combination thereof, wherein $2 < c \leq 5$; and Y is a halogen, wherein $0 \leq d \leq 1$.

[014] Also disclosed herein is a secondary battery comprising any of the disclosed herein cathode electrodes. In still further aspects, the disclosed herein secondary batteries further comprise an anode electrode and an electrolyte.

[015] In further aspects, disclosed herein is a method of making any of the disclosed herein cathode electrodes wherein the method comprises: a) forming a mixture comprising an alkali metal or an alkaline-earth metal, one or more transition metals, and a chalcogen-group element; (b) heating the mixture to form an active material represented by M^1M^2X , wherein M^1 is an alkali metal ion or an alkali-earth metal ion, wherein M^2 comprises one or more transition metal ions, and wherein X comprises at least one chalcogen anion, and wherein M^1 , M^2 , and X are present in a predetermined ratio.

[016] Still further disclosed herein are methods of making any of the secondary batteries disclosed herein.

[017] Additional advantages will be set forth in part in the description which follows, and in part will be obvious from the description or can be learned by practice of the aspects described below. The advantages described below will be realized and attained by means of the chemical compositions, methods, and combinations thereof, particularly pointed out in the appended claims. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as claimed.

BRIEF DESCRIPTION OF DRAWINGS

[018] FIGURES 1A-1B show cathode design strategies. FIG. 1A shows an illustration of the advantages of anion-redox cathodes. FIG. 1B shows the comparative electrochemical performance of the reported cathodes for Na ion batteries.

[019] FIGURES 2A-2E show the redox behavior of Na_6MS_4 . FIG. 2A shows a crystal structure of Na_6CoS_4 . FIG. 2B shows redox energies of the transition-metal ions with respect to the top of the S^{2-} :2p band. FIG. 2C shows an evolution of pDOS with various transition metals. The Na, S, Zn, Mn, Co, and Fe projections are colored, respectively, in red, grey, light green, purple, blue, and yellow. FIG. 2D shows voltage profiles of the compositions synthesized vs. Na metal at a C/10 rate between 1.2 and 2.8 V in the first cycle. FIG. 2E shows an illustration of the structure of Na_6MS_4 .

[020] FIGURES 3A-3G show the SEM morphology of $\text{Na}_6\text{CoS}_4@\text{C}$ (FIGs. 3A-3B). SEM of $\text{Na}_6\text{CoS}_4@\text{C}$ with the corresponding elemental mapping images of C, Co, Na, and S (FIG. 3C).

[021] FIGURE 4 is an XRD pattern of $\text{Na}_6\text{CoS}_4@\text{C}$.

[022] FIGURE 5 is an XRD pattern of $\text{Na}_6\text{CoS}_4@\text{C}$ prepared by the reported method with the reaction between S, Co, and Na_2CO_3 under an H_2 atmosphere at 725 °C for 3 h.

[023] FIGURES 6A-6B show the SEM images of $\text{Na}_6\text{FeS}_4@\text{C}$ at various magnifications.

[024] FIGURE 7 is the SEM images and corresponding elemental mapping of $\text{Na}_6\text{FeS}_4@\text{C}$.

[025] FIGURE 8 is an XRD pattern of $\text{Na}_6\text{FeS}_4@\text{C}$.

[026] FIGURES 9A-9B show the SEM images of $\text{Na}_6\text{MnS}_4@\text{C}$ at various magnifications.

[027] FIGURE 10 is the SEM images and corresponding elemental mapping of $\text{Na}_6\text{MnS}_4@\text{C}$.

[028] **FIGURE 11** is an XRD pattern of $\text{Na}_6\text{MnS}_4@\text{C}$.

[029] **FIGURES 12A-12B** show the SEM images of $\text{Na}_6\text{ZnS}_4@\text{C}$ at various magnifications.

[030] **FIGURE 13** is the SEM images and corresponding elemental mapping of $\text{Na}_6\text{ZnS}_4@\text{C}$.

[031] **FIGURE 14** is an XRD pattern of $\text{Na}_6\text{ZnS}_4@\text{C}$.

[032] **FIGURES 15A-15G** show the electrochemical behavior of $\text{Na}_6\text{CoS}_4@\text{C}$. FIG. 15A- Long-term cycling performance of $\text{Na}_6\text{MS}_4@\text{C}$ cathodes. FIG. 15B- The corresponding discharge/charge voltage profiles of $\text{Na}_6\text{CoS}_4@\text{C}$ cathode. FIG. 15C- Rate performance of $\text{Na}_6\text{CoS}_4@\text{C}$ cathode at various C rates. FIG. 15D- Cycling performance of $\text{Na}_6\text{CoS}_4@\text{C}$ coin cell with a high active material loading (5 mg cm^{-2}). Cycling performances of $\text{Na}_6\text{CoS}_4@\text{C}$ pouch cell with FIG. 15E- a low active material loading and FIG. 15F- a high active material loading and lean electrolyte conditions. FIG. 15G- Cycling performances of anode-free $\text{Ni}|| \text{Na}_6\text{CoS}_4@\text{C}$ cell.

[033] **FIGURE 16** shows the CV curves of $\text{Na}_6\text{CoS}_4@\text{C}$ cathode at 0.1 mV s^{-1} in a potential window from 1.2 to 2.8 V.

[034] **FIGURES 17A-17D** illustrate the behavior of $\text{Na}_6\text{CoS}_4@\text{C}$. FIG. 17A- Charge and discharge curves of a $\text{Na}_6\text{CoS}_4@\text{C}$ coin cell in the initial cycle and FIG. 17B- the corresponding diffraction patterns. FIG. 17C- CV curves of a $\text{Na}_6\text{CoS}_4@\text{C}$ coin cell in the first two cycles and FIG. 17D- the corresponding time sequence of Raman spectra.

[035] **FIGURES 18A-18F** show the characterizations of cycled $\text{Na}_6\text{CoS}_4@\text{C}$. FIG. 18A- High-resolution TEM images of fresh $\text{Na}_6\text{CoS}_4@\text{C}$, FIGs. 18B-18D- fully charged $\text{Na}_6\text{CoS}_4@\text{C}$, and FIG. 18E- fully discharged $\text{Na}_6\text{CoS}_4@\text{C}$. FIG. 18F- S 2p spectra of the fresh, fully charged, and fully discharged $\text{Na}_6\text{CoS}_4@\text{C}$ cathode.

[036] **FIGURE 19** shows the Co 2p spectra of the fresh, fully charged, and fully discharged $\text{Na}_6\text{CoS}_4@\text{C}$ cathode.

[037] **FIGURE 20** shows the high-resolution TEM images of $\text{Na}_6\text{CoS}_4@\text{C}$ at a fully discharged state.

[038] **FIGURE 21** shows the TEM images of $\text{Na}_6\text{CoS}_4@\text{C}$ at the initial state and the corresponding elemental mapping images of C, Na, S, and Co.

[039] **FIGURE 22** shows the TEM images of $\text{Na}_6\text{CoS}_4@\text{C}$ at a fully discharged state and the corresponding elemental mapping images of C, Na, S, and Co.

[040] **FIGURE 23** shows a schematic of the conversion of $\text{Na}_6\text{CoS}_4@\text{C}$. A conversion from high crystallinity to an amorphous structure

[041] **FIGURE 24** shows the cycling performance of the $\text{Na}_6\text{CoS}_4@\text{C}$ coin cell in a low-concentration electrolyte of 1 M NaFSI in DME.

[042] **FIGURE 25** shows the evolution of the pDOS of Na_6CoS_4 with Na extraction (charge).

[043] **FIGURE 26** is a battery cycle performance diagram of the battery positive electrode Na_6CoS_4 in the present invention under a current density of 0.2A/g.

[044] **FIGURE 27** is a capacity-voltage curve diagram of a positive electrode material of the battery positive electrode Na_6CoS_4 in the present invention.

[045] **FIGURE 28** is a battery cycle performance diagram of the battery positive electrode Na_6FeS_4 in the present invention under a current density of 0.2A/g.

[046] **FIGURE 29** is a capacity-voltage curve diagram of a positive electrode material of the battery positive electrode Na_6FeS_4 in the present invention.

[047] **FIGURE 30** is a cycle performance diagram of a comparative example $\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NFM).

[048] **FIGURE 31** is a capacity-voltage curve of the comparative example $\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NFM).

[049] The accompanying figures, which are incorporated in and constitute a part of this specification, illustrate several aspects described below.

DETAILED DESCRIPTION

[050] The present invention can be understood more readily by reference to the following detailed description, examples, drawings, and claims, and their previous and following description. However, before the present articles, systems, and/or methods are disclosed and described, it is to be understood that this invention is not

limited to the specific or exemplary aspects of articles, systems, and/or methods disclosed unless otherwise specified, as such can, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular aspects only and is not intended to be limiting.

[051] The following description of the invention is provided as an enabling teaching of the invention in its best, currently known aspect. To this end, those skilled in the relevant art will recognize and appreciate that many changes can be made to the various aspects of the invention described herein while still obtaining the beneficial results of the present invention. It will also be apparent that some of the desired benefits of the present invention can be obtained by selecting some of the features of the present invention without utilizing other features. Accordingly, those of ordinary skill in the pertinent art will recognize that many modifications and adaptations to the present invention are possible and may even be desirable in certain circumstances and are a part of the present invention. Thus, the following description is again provided as illustrative of the principles of the present invention and not in limitation thereof.

DEFINITIONS

[052] As used herein, the terms "optional" or "optionally" mean that the subsequently described event or circumstance can or cannot occur and that the description includes instances where said event or circumstance occurs and instances where it does not.

[053] It is appreciated that certain features of the disclosure, which are, for clarity, described in the context of separate aspects, can also be provided in combination in a single aspect. Conversely, various features of the disclosure, which are, for brevity, described in the context of a single aspect, can also be provided separately or in any suitable subcombination.

[054] As used in the description and the appended claims, the singular forms "a," "an," and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, a reference to "a salt" includes two or more such salts and a reference to "a battery" includes two or more such batteries and the like.

[055] It is also to be understood that the terminology used herein is for the purpose of describing particular aspects only and is not intended to be limiting. As used in the specification and in the claims, the term “comprising” can include the aspects “consisting of” and “consisting essentially of.” Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. In this specification and in the claims which follow, reference will be made to a number of terms that shall be defined herein.

[056] For the terms “for example” and “such as,” and grammatical equivalences thereof, the phrase “and without limitation” is understood to follow unless explicitly stated otherwise. It is further understood that these phrases are used for explanatory purposes only. It is further understood that the term “exemplary,” as used herein, means “an example of” and is not intended to convey an indication of a preferred or ideal aspect.

[057] The expressions “ambient temperature” and “room temperature” as used herein are understood in the art and refer generally to a temperature from about 20 °C to about 35 °C.

[058] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the disclosure are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard deviation found in their respective testing measurements. Furthermore, when numerical ranges of varying scope are set forth herein, it is contemplated that any combination of these values, inclusive of the recited values, may be used. Further, ranges can be expressed herein as from “about” one particular value and/or to “about” another particular value. When such a range is expressed, another aspect includes from the one particular value and/or to the other particular value.

[059] Similarly, when values are expressed as approximations, by use of the antecedent “about,” it will be understood that the particular value forms another aspect. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint and independently of the other

endpoint. Unless stated otherwise, the term “about” means within 5% (e.g., within 2% or 1%) of the particular value modified by the term “about.”

[060] All disclosed values also include values that fall within $\pm 10\%$ variation from the disclosed value unless otherwise indicated or inferred. In other words, if a range of 1 to 10 is disclosed, then a range of about 1 to about 10 is disclosed. In such aspects, it is understood that the amount or value in question can be the exact value or a value that provides equivalent results or effects as recited in the claims or taught herein. That is, amounts, sizes, formulations, parameters, and other quantities and characteristics include both exact values but also approximate, larger or smaller values as desired, reflecting tolerances, conversion factors, rounding, measurement error, and the like, and other factors known to those of skill in the art such that equivalent results or effects are obtained. In some circumstances, the value that provides equivalent results or effects cannot be reasonably determined. In general, an amount, size, formulation, parameter, or other quantity or characteristic is “about,” “approximate,” or “at or about,” whether or not expressly stated to be such. Where “about,” “approximate,” or “at or about” is used before a quantitative value, the parameter also includes the specific quantitative value itself unless expressly stated otherwise.

[061] As used herein, the term or phrase “effective,” “effective amount,” or “conditions effective to” refers to such amount or condition that is capable of performing the function or property for which an effective amount or condition is expressed. As will be pointed out below, the exact amount or particular condition required will vary from one aspect to another, depending on recognized variables such as the materials employed and the processing conditions observed. Thus, it is not always possible to specify an exact “effective amount” or “condition effective to.” However, it should be understood that an appropriate, effective amount will be readily determined by one of ordinary skill in the art.

[062] When a range is expressed, a further aspect includes from the one particular value and to the other particular value. For example, where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included in the disclosure, e.g., the phrase “x to y” includes the range from ‘x’ to ‘y’ as well as the range greater than ‘x’ and less than ‘y’. The range can also be

expressed as an upper limit, e.g., 'x, y, z, or less' and should be interpreted to include the specific ranges of 'x,' 'y,' 'z,' 'about x,' 'about y,' and 'about z' as well as the ranges of 'less than x,' 'less than y, or 'less than z,' or 'less than about x,' 'less than about y, and 'less than about z.' Likewise, the phrase 'x, y, z, or greater' should be interpreted to include the specific ranges of 'x,' 'y,' 'z,' 'about x,' 'about y,' and 'about z' as well as the ranges of 'greater than x,' greater than y,' 'greater than z,' or 'greater than about x,' greater than about y,' 'greater than about z.' In addition, the phrase " 'x' to 'y'," where 'x' and 'y' are numerical values, also includes "about 'x' to about 'y'."

[063] Such a range format is used for convenience and brevity and, thus, should be interpreted flexibly to include not only the numerical values explicitly recited as the limits of the range but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. To illustrate, a numerical range of " 0.1% to 5%" should be interpreted to include not only the explicitly recited values of 0.1% to 5% but also include individual values (e.g., 1%, 2%, 3%, and 4%) and the sub-ranges (e.g., 0.5% to 1.1%; 5% to 2.4%; 0.5% to 3.2%, and 0.5% to 4.4%, and other possible sub-ranges) within the indicated range.

[064] Throughout this disclosure, various aspects of the invention can be presented in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the invention. Accordingly, the description of a range should be considered to have specifically disclosed all the possible subranges as well as individual numerical values within that range. For example, a description of a range such as from 1 to 6 should be considered to have specifically disclosed subranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6, etc., as well as individual numbers within that range, for example, 1, 2, 2.7, 3, 4, 5, 5.3, 6 and any whole and partial increments therebetween. This applies regardless of the breadth of the range.

[065] In still further aspects, when the specific values are disclosed between two end values, it is understood that these end values can also be included.

[066] In still further aspects, when the range is given, and exemplary values are provided, it is understood that any ranges can be formed between any exemplary values within the broadest range. For example, if individual numbers 1, 2, 3, 4, 5, 6, 7, etc. are disclosed, then the ranges 1-7, 2-7, 3-7, 4-7, 5-7, 6-7, 1-6, 1-5, 1-4, 1-3, 1-2, 2-6, 2-5, etc. are also disclosed.

[067] References in the specification and concluding claims to parts by weight of a particular element or component in a composition denote the weight relationship between the element or component and any other elements or components in the composition or article for which a part by weight is expressed. Thus, in a mixture containing 2 parts by weight of component X and 5 parts by weight, components Y, X, and Y are present at a weight ratio of 2:5 and are present in such a ratio regardless of whether additional components are contained in the mixture.

[068] A weight percent (wt.%) of a component, unless specifically stated to the contrary, is based on the total weight of the formulation or composition in which the component is included.

[069] It will be understood that when an element is referred to as being "connected" or "coupled" to another element, it can be directly connected or coupled to the other element, or intervening elements may be present. In contrast, when an element is referred to as being "directly connected" or "directly coupled" to another element, there are no intervening elements present. Other words used to describe the relationship between elements or layers should be interpreted in a like fashion (e.g., "between" versus "directly between," "adjacent" versus "directly adjacent," "on" versus "directly on").

[070] As used herein, the term "and/or" includes any and all combinations of one or more of the associated listed items.

[071] It will be understood that the terms "first," "second," etc., may be used herein to describe various elements, components, regions, layers, and/or sections. These elements, components, regions, layers, and/or sections should not be limited by these terms. These terms are only used to distinguish one element, component, region, layer, or section from another element, component, region, layer, or section. Thus, a first element, component, region, layer, or section discussed below could be

termed a second element, component, region, layer, or section without departing from the teachings of example embodiments.

[072] As used herein, the term "substantially" means that the subsequently described event or circumstance completely occurs or that the subsequently described event or circumstance generally, typically, or approximately occurs.

[073] Still further, the term "substantially" can, in some aspects, refer to at least about 80 %, at least about 85 %, at least about 90 %, at least about 91 %, at least about 92 %, at least about 93 %, at least about 94 %, at least about 95 %, at least about 96 %, at least about 97 %, at least about 98 %, at least about 99 %, or about 100 % of the stated property, component, composition, or other condition for which substantially is used to characterize or otherwise quantify an amount.

[074] In other aspects, as used herein, the term "substantially free," when used in the context of a composition or component of a composition that is substantially absent, is intended to refer to an amount that is then about 1 % by weight, e.g., less than about 0.5 % by weight, less than about 0.1 % by weight, less than about 0.05 % by weight, or less than about 0.01 % by weight of the stated material, based on the total weight of the composition.

[075] As used herein, the terms "substantially identical reference composition," "substantially identical reference article," or "substantially identical reference electrochemical cell" refer to a reference composition, article, or electrochemical cell comprising substantially identical components in the absence of an inventive component. In another exemplary aspect, the term "substantially," in, for example, the context "substantially identical reference composition," or "substantially identical reference article," or "substantially identical reference electrochemical cell," refers to a reference composition, article, or an electrochemical cell comprising substantially identical components and wherein an inventive component is substituted with a common in the art component.

[076] While aspects of the present invention can be described and claimed in a particular statutory class, such as the system statutory class, this is for convenience only and one of ordinary skill in the art will understand that each aspect of the present invention can be described and claimed in any statutory class. Unless

otherwise expressly stated, it is in no way intended that any method or aspect set forth herein be construed as requiring that its steps be performed in a specific order. Accordingly, where a method claim does not specifically state in the claims or descriptions that the steps are to be limited to a specific order, it is in no way intended that an order be inferred in any respect. This holds for any possible non-express basis for interpretation, including matters of logic with respect to the arrangement of steps or operational flow, plain meaning derived from grammatical organization or punctuation, or the number or type of aspects described in the specification.

[077] The present invention may be understood more readily by reference to the following detailed description of various aspects of the invention and the examples included therein and to the Figures and their previous and following description.

CATHODE ELECTRODES

[078] In the realm of energy storage, the rapid evolution of battery technologies has ignited a fervent quest for safer, more efficient, sustainable solutions (1-3). For battery chemistry to enter the market for energy storage applications like electric vehicles (EVs), they need to satisfy some critical parameters, such as an energy density of $> 150 \text{ Wh kg}^{-1}$ with > 500 cycles. As lithium-ion batteries (LIBs) continue to dominate the market, concerns about the availability and cost of lithium resources have spurred interest in alternative battery chemistries. Among the emerging contenders, sodium-ion batteries (SIBs) have recently crossed this threshold and have begun to be employed in EVs due to their potential to offer performance comparable to lithium-ion batteries while utilizing more abundant sodium resources (4-6). The cathode, a pivotal component of SIBs, plays a crucial role in determining the overall performance and characteristics of the batteries. For many years, cathode materials for SIBs mainly relied solely on transition metal (cationic) redox, resulting in a limited capacity and energy density (FIG. 1A). Therefore, it is critical to look into approaches that can significantly enhance the energy density and lifespan of SIBs.

[079] In recent years, the sulfur cathode with a conversion redox reaction has emerged as a potential candidate for high-energy-density SIBs. However, such

cathodes with a conversion redox suffer from unstable redox chemistry during the conversion, including the polysulfide shuttling effect, leading to a limited lifespan. Apart from classical intercalation chemistry and conversion chemistry, there are materials that are a hybrid, i.e., anionic-redox materials. There has been immense interest in recent years in anionic redox in LIBs with the electrochemical participation of sulfur to offer higher capacities, such as Li-rich layered sulfides $\text{Li}_{1.33}\text{Ti}_{0.57}\text{Fe}_{0.3}\text{S}_2$ (7). It has been shown that FeS_x and MoS_x can undergo anion redox. However, these materials do not contain sodium and thus (or any other alkali metal) would necessitate pairing them with a Na-metal anode (or other corresponding alkali-metal anode), which is known to have poor reversibility. Therefore, it is preferable to have a cathode that contains sodium (or other alkali metals as disclosed herein) in it as it can allow the use of traditional anodes like hard carbon or even anode-free cell designs. An early effort by Shadike and co-workers reported reversible $\text{S}^{2-}/\text{S}_2^{2-}$ redox in layered O3-type NaCrS_2 cathode (8), which delivers a capacity of 103 mAh g^{-1} . NaCrS_2 with anionic sulfur redox provides new insights to bring forth high-capacity cathodes for SIBs. In such materials, sulfur exists fully or partially as dimerized $\text{S}^-\text{-S}^-$ (or S_2^{2-}) pairs that break into the standard S^{2-} state upon electrochemical insertion of Na (FIG. 1B). However, the anionic redox activity is only partly reversible in such materials, resulting in rapid capacity fade (9). Therefore, there is much appetite to develop stable cathodes with high capacities for SIBs, potentially involving anionic redox.

[080] In certain aspects, disclosed herein are novel cathode electrode materials that are shown to overcome these deficiencies.

[081] In certain aspects, disclosed herein is a cathode electrode for a reversible battery comprising an active material comprising an alkali metal ion or alkaline-earth metal ion and at least one or more transition metal chalcogenides, and wherein active redox species comprise anions. Yet, in other aspects, the active redox species are substantially anions. Yet, in other aspects, the active redox species are anions.

[082] In certain aspects, the anion redox species comprise chalcogen anion.

[083] In certain aspects, the active material comprises an alkali metal ion and at least one or more transition metal chalcogenides. In other aspects, the active

material comprises an alkaline-earth metal ion and at least one or more transition metal chalcogenides. In yet other aspects, the active material can comprise an alkali metal ion and at least one or more transition metal chalcogenides doped with an alkaline-earth metal. In still further aspect, when the alkaline-earth metal is a dopant, it can be present in an amount of about 0.1 to about 45 wt%, including exemplary values of about 0.5 wt%, about 1 wt%, about 5 wt%, about 10 wt%, about 15 wt%, about 20 wt%, about 25 wt%, about 30 wt%, about 35 wt%, and about 40 wt%. It is understood that the dopant can be present in any amount that falls between any two foregoing values, or it can fall in any range formed by any two foregoing values. For example, and without limitations, the dopant can be present in an amount of about 0.1 to about 43 wt%, about 0.1 to about 40 wt%, about 0.1 to about 30 wt%, about 0.1 to about 20 wt%, about 0.1 to about 10 wt%, about 0.1 to about 5 wt%, about 0.1 to about 1 wt%, about 0.1 to about 0.5 wt%, and so on.

[084] In still further aspects, the active material is substantially crystalline. Yet in still further aspects, the active material is crystalline.

[085] In still further aspects, the active material can be represented by M^1M^2X . In such exemplary aspects, M^1 represents the working/stored/active ion(s) containing a positive charge, M^2 is the structural ion(s) containing a positive charge, and X is the counter ion which starts with a negative charge but undergoes redox (change in charge) as M^1 is inserted/removed from the structure. In yet still further aspects, M^1 is an alkali or an alkaline-earth metal ion. In yet still further aspects, M^1 comprises Li, Na, K, or a combination thereof. Yet in still further aspects, M^1 can be Ca, Mg, or a combination thereof. In still further aspects M^2 comprises at least one transition metal ion. In such exemplary and unlimiting aspects, M^2 can comprise Co, Fe, Mn, Ni, V, Ti, Cr, Cu, Zr, Nb, Ta, Mo, W, Pd, Pt, Re, Cd, or a combination thereof. In still further aspects, X comprises a chalcogen ion. For example, and without limitations, wherein X can comprise S, Se, Te, O, or a combination thereof. In still further aspects, M^1 , M^2 , and X are present in a predetermined ratio.

[086] In still further aspects, the active material can further comprise Y and is represented by M^1M^2XY , wherein Y comprises a halogen and wherein M^1 , M^2 , X, and Y are present in a predetermined ratio. It is understood that in these exemplary

aspects, Y is the supporting ion with a negative charge that may or may not undergo redox.

[087] In certain aspects, and as disclosed above, the active material can further comprise a dopant. In such exemplary and unlimiting aspects, M^2 comprises a dopant comprising one or more of, but not limited to, Mg, Ba, Ca, Sr, Al, B, Ga, Si, Ge, As, Zn, Sn, Sb, In, or any combination thereof. In still further aspects, the dopant can be present in an amount of about 0.1 to about 45 wt%, including exemplary values of about 0.5 wt%, about 1 wt%, about 5 wt%, about 10 wt%, about 15 wt%, about 20 wt%, about 25 wt%, about 30 wt%, about 35 wt%, and about 40 wt%. It is understood that the dopant can be present in any amount that falls between any two foregoing values, or it can fall in any range formed by any two foregoing values. For example, and without limitations, the dopant can be present in an amount of about 0.1 to about 43 wt%, about 0.1 to about 40 wt%, about 0.1 to about 30 wt%, about 0.1 to about 20 wt%, about 0.1 to about 10 wt%, about 0.1 to about 5 wt%, about 0.1 to about 1 wt%, about 0.1 to about 0.5 wt%, and so on.

[088] In still further aspects, the active material is represented by $M_a^1 M_b^2 X_c Y_d$. In certain exemplary and unlimiting aspects, M^1 can be Na (but it is understood that it can also be Li, K, Ca, or Mg or combinations thereof) and $2 \leq a \leq 7$, including exemplary values of about 2, about 2.1, about 2.5, about 2.7, about 3, about 3.2, about 3.5, about 3.7, about 4, about 4.2, about 4.5, about 4.7, about 5, about 5.2, about 5.5, about 5.7, about 6, about 6.2, about 6.5, about 6.7, and about 7. In still further aspects, a can have a value that falls within any range formed by the mentioned above values, for example, it can be in a range of about 2.1- about 6.9, about 2.5- about 6.3, about 2- about 6, about 3- about 7, about 3- about 6, about 4- about 7, about 2- about 6.4, and so on.

[089] In further aspects, M^2 is one of Co, Fe, Mn, Ni, V, Ti, Cr, Cu, Zr, Nb, Ta, Mo, W, Pd, Pt, Re, Cd, or a combination thereof, $0 < b \leq 2$, including exemplary values of about 0.01, about 0.1, about 0.2, about 0.3, about 0.4, about 0.5, about 0.6, about 0.7, about 0.8, about 0.9, about 1, about 1.1, about 1.2, about 1.3, about 1.4, about 1.5, about 1.6, about 1.7, about 1.8, about 1.9, and about 2. In still further aspects, b can have a value that falls within any range formed by the mentioned above values, for example, it can be in a range of about 0.01- about 2, about 0.1- about 2, about

0.5- about 2, about 0.7- about 2, about 1- about 2, about 1.2- about 2, about 1.5- about 2, and so on.

[090] In still further aspects, X is one or more of S, Se, Te, O, or a combination thereof and $2 < c \leq 5$, including exemplary values of about 2.01, about 2.1, about 2.2, about 2.3, about 2.4, about 2.5, about 2.6, about 2.7, about 2.8, about 2.9, about 3, about 3.1, about 3.2, about 3.3, about 3.4, about 3.5, about 3.6, about 3.7, about 3.8, about 3.9, about 4, about 4.1, about 4.2, about 4.3, about 4.4, about 4.5, about 4.6, about 4.7, about 4.8, about 4.9, and about 5. In still further aspects, c can have a value that falls within any range formed by the mentioned above values, for example, it can be in a range of about 2.01- about 5, about 2.1- about 5, about 2.5- about 5, about 3- about 5, about 3.5- about 5, about 4- about 5, about 4.5- about 5, and so on.

[091] In still further aspects, Y is a halogen, and wherein $0 \leq d \leq 1$, including exemplary values of 0, about 0.01, about 0.1, about 0.2, about 0.3, about 0.4, about 0.5, about 0.6, about 0.7, about 0.8, about 0.9, and about 1. It is understood that when d is zero, Y is not present. In yet still further aspects, Y can be present in any amount that falls between any two foregoing values. In still further aspects, Y can be present in an amount that falls in any range formed by any two foregoing values. For example, d can be in a range of about 0.001- about 1, about 0.01- about 1, about 0.05- about 1, about 0.1- about 1, about 0.1- about 0.9, about 0.1- about 0.8, about 0.1- about 0.5, and so on. In still further aspects, when $d > 0$, Y is Cl, Br, I, F, or a combination thereof.

[092] In still further aspects, the M^2 can further comprise a dopant comprising, but not limited to, one or more of Mg, Ba, Ca, Sr, Al, B, Ga, Si, Ge, As, Zn, Sn, Sb, In, or any combination thereof. It is understood that dopants can be present in any amount, as disclosed above.

[093] In yet still further aspects, the M^1 is Na, while the M^2 is Co, Fe, Mn, or a combination thereof. In yet still further aspects, X is S or Se or Te, O, or a combination thereof. In yet still further aspects, the active material comprises Na_6CoS_4 . In still further aspects, the active material comprises Na_6FeS_4 . In still further aspects, the active material comprises Na_6MnS_4 .

[094] In still further aspects, the active material can further comprise a conductive agent. It is understood that the conductive agent can comprise any known conductive materials in the art of electrochemical cells. In some aspects, the conductive agent can comprise one or more of carbon black, acetylene black, carbon nanotubes, graphene, graphite, modified and unmodified carbon, conductive polymers, conductive oxides, conductive ceramics, or any combination thereof. It is understood that any conductive polymers can be used, for example, conductive polymers can comprise polyacetylene (PA), polypyrrole (PPy), polythiophene (PTH) polyindole (PI), polyaniline, poly(3,4-ethylenedioxythiophene) (PEDOT), poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), polyfuran (PF), poly(phenylenevinylene) (PPV), poly(para-phenylene) (PPP), polyacrylonitrile (PAN), or any combinations thereof.

[095] In still further aspects, the active material further comprises a binder. Any known art of battery binders can be used. For example, the binders can comprise poly(vinylidene fluoride) (PVDF), polyethylene oxide, cellulose, carboxymethylcellulose, polytetrafluoroethylene, styrene-butadiene rubber, polyvinylpyrrolidone (PVP), or any combinations hereof.

BATTERIES

[096] Disclosed herein are secondary batteries that comprise any of the disclosed above cathode electrodes without limitations. Some exemplary cathode materials and batteries comprising the same are shown in the examples below. In still further exemplary and unlimiting aspects, the battery is a sodium-ion battery. It is understood, however, that similar materials can be formed for lithium-ion, potassium-ion, magnesium-ion, or calcium-ion batteries. In such exemplary aspects, M^1 would comprise Li, K, Mg, or Ca, respectively.

[097] In some exemplary and unlimiting aspects, the cathode materials present in the sodium-ion battery can comprise Na_6CoS_4 , Na_6FeS_4 , or Na_6MnS_4 or a combination thereof.

[098] In still further aspects, the battery further comprises an anode electrode and an electrolyte.

[099] In certain aspects, the electrolyte is a liquid electrolyte comprising a salt and a solvent. In such exemplary and unlimiting aspects, the salt comprises a cation that is a cation of alkali and/or alkaline-earth metal present in the complex. For example, for sodium-ion batteries, the salt can comprise one or more of sodium fluorophosphate (NaPF₆), sodium fluoroborate (NaBF₄), sodium tetraphenylborate (NaBPh₄), sodium bis(fluorosulfonyl)imide (NaFSI), sodium bis(trifluoromethanesulfonyl)imide (NaTFSI), sodium (fluorosulfonyl)(trifluoromethanesulfonyl)imide (NaFTFSI), sodium perchlorate (NaClO₄), sodium nitrate (NaNO₃), sodium 4,5-dicyano-2-(trifluoromethyl)imidazole (NaTDI), sodium 4,5-dicyano-2-(pentafluoromethyl)imidazole (NaPDI), and sodium difluorooxalato borate (NaDFOB), or any combination thereof. Yet in the aspects where the battery is a Li-ion battery or potassium-ion battery, any of the mentioned above salts with Li or K cation (instead of Na cation) can be utilized.

[100] In still further aspects, the solvent comprises one or more of ethylene carbonate (EC), 1,2-Dimethoxyethane (DME), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), 1,2-Dimethoxyethane (DME), fluoroethylene carbonate (FEC), tetrahydrofuran (THF), diethylene glycol dimethyl ether (Diglyme), triethylene glycol dimethyl ether (TDEM), tetraethylene glycol dimethyl ether (TEGDME), and vinylene carbonate (VC), Bis(2,2,2-trifluoroethyl) ether (BTFE), 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropylether (TTE), tris(2,2,2-trifluoroethyl) orthoformate (TFEO), trimethylphosphate (TMP), triethylphosphate (TEP), or any combination hereof. It is understood that the electrolyte can comprise one solvent or a mixture of two or more solvents. If more than one solvent is present, such solvents can be in any weight or volume ratio relative to each other.

[101] In still further aspects, the salt can be present in the electrolyte in any amount that provides the desired conductivity and can be dictated by the solubility of the salt in a specific solvent. In certain aspects, the salt is present in an amount of about 0.01 M to about 3 M, including exemplary values of about 0.05 M, about 0.1 M, about 0.2 M, about 0.3 M, about 0.4 M, about 0.5 M, about 0.6 M, about 0.7 M, about 0.8 M, about 0.9 M, about 1 M, about 1.1 M, about 1.2 M, about 1.3 M, about 1.4 M, about 1.5 M, about 1.6 M, about 1.7 M, about 1.8 M, about 1.9 M, about 2 M, about 2.1 M, about 2.2 M, about 2.3 M, about 2.4 M, about 2.5 M, about 2.6 M, about 2.7

M, about 2.8 M, and about 2.9 M. In still further aspects, the salt can be present in any amount between any two foregoing values. In yet still further aspects, the salt can be present in an amount that falls within a range formed by any two values described above. For example, the salt can be present in an amount of about 0.05 M to about 3 M, about 0.1 M to about 3 M, about 0.5 M to about 3 M, about 1 M to about 3 M, about 1.5 M to about 3 M, about 2 M to about 3 M, and so on. It is understood, however, that in certain aspects, when the solubility of the salt allows it, the salt can be present in an amount higher than about 3 M, higher than about 3.5 M, higher than about 4 M, higher than about 4.5 M, or even higher than about 5 M.

[102] In still further aspects, it is understood that the salt amount can be presented in different units, such as molality or weight (wt) %. In aspects where the salt amount is presented in wt%, the weight percent of the salt is calculated based on the total weight of the electrolyte.

[103] In still further aspects, the battery can comprise any solid or hybrid electrolyte known in the art. In certain aspects, the electrolyte is a solid electrolyte and comprises an inorganic ceramic/glass-ceramic, organic polymer, and ceramic-polymer composite electrolytes. For example, and without limitations, for sodium-ion batteries, the solid electrolyte can comprise doped and undoped NASICON-type compounds, perovskite-type and anti-perovskite-type compounds, nitrides, oxynitrides, beta-alumina, Cryolite-type, argyrodite-type, or polymer-based electrolytes, or ceramic-polymer composite electrolytes, or any combination thereof. If the electrolyte is polymer-based electrolytes, such electrolytes can further comprise an alkali metal, an alkaline-earth metal salt, or a combination thereof. In still further aspects, any known in the art anode materials can be used. For example, and without limitations, the anode electrode comprises one or more metallic alkali and/or alkaline earth foils, alkali and/or alkaline earth powder, alkali and/or alkaline earth meshes, alkali and/or alkaline earth alloys, carbon materials, non-alkali and/or non-alkaline earth metal alloys, nonmetal alloys, compound materials, or any combination thereof. Yet in still further aspects, the battery can be “anodeless.” In such aspects, the anode electrode is a current collector for an alkali metal or alkaline earth metal deposition during a plating step. In such aspects, the current collectors can be a metal or another conductive material, such as (but not limited to) nickel (Ni),

copper (Cu), aluminum (Al), iron (Fe), stainless steel, or conductive carbon materials. The current collector may be a foil, a foam, or a polymer substrate coated with a conductive material.

[104] In still further aspects, where the battery is a sodium-ion battery, the anode electrode comprises any known in the art elemental or compound anode suitable for sodium-ion battery applications.

[105] In still further aspects, where batteries comprise a liquid electrolyte, for example, the battery can further comprise a separator. In such aspects, any known in the art separators that are capable of achieving the desired results can be used. For example, and without limitations, the separators can comprise glass fiber, a porous polymer film (e.g., polyethylene- or polypropylene-based material) with or without a ceramic coating, or a composite (e.g., a porous film of inorganic particles and a binder). One exemplary polymeric separator is a polyethylene (PE) membrane. Another exemplary polymeric separator is a polypropylene (PP) membrane. Another exemplary polymeric separator is a Celgard® 3501 surfactant-coated polypropylene membrane. The separator may be infused with any of the disclosed herein electrolytes.

[106] In still further aspects, the batteries disclosed herein exhibit a specific capacity of about 100 mAh g⁻¹ to about 600 mAh g⁻¹ at a discharge rate of at least about 0.1C. For example, the batteries can exhibit a specific capacity of about 100 mAh g⁻¹ to about 600 mAh g⁻¹, including exemplary values of about 120 mAh g⁻¹, about 150 mAh g⁻¹, about 200 mAh g⁻¹, about 250 mAh g⁻¹, about 300 mAh g⁻¹, about 350 mAh g⁻¹, about 400 mAh g⁻¹, about 450 mAh g⁻¹, about 500 mAh g⁻¹, about 550 mAh g⁻¹, and about 590 mAh g⁻¹ at a discharge rate of at least about 0.1C, of at least about 0.2C, of at least about 0.5C, of at least about 1C, of at least about 2C, of at least about 3C, of at least about 4C, of at least about 5C, and so on. It is understood that the specific capacity can fall between any disclosed above values or can fall within any range formed by the disclosed above values. In certain aspects, the batteries disclosed herein exhibit a specific capacity of about 100 mAh g⁻¹ to about 600 mAh g⁻¹, about 150 mAh g⁻¹ to about 600 mAh g⁻¹, about 200 mAh g⁻¹ to about 600 mAh g⁻¹, about 300 mAh g⁻¹ to about 600 mAh g⁻¹, about 400 mAh g⁻¹ to about 600 mAh g⁻¹,

about 500 mAh g⁻¹ to about 600 mAh g⁻¹, and so on at any of the disclosed above discharge rates.

[107] In still further aspects, the batteries disclosed herein can exhibit a capacity retention of at least about 75% over at least about 200 cycles. Yet in still further aspects, the batteries disclosed herein can exhibit a capacity retention of at least about 75% over at least about 500 cycles. In yet still further aspects, the battery exhibits a capacity retention of at least about 75%, at least about 80%, at least about 85%, at least about 90%, at least about 95%, at least about 99%, over at least about 500 cycles. It is understood that such capacity retention can also be observed for at least about 700 cycles, at least about 1,000 cycles, at least about 5,000 cycles, at least about 10,000 cycles, or at least about 20,000 cycles.

[108] In still further aspects, the batteries disclosed herein can exhibit a Coulombic efficiency greater than about 80%, greater than about 85%, greater than about 90%, greater than about 95%, or greater than about 99% over at least about 500 cycles. It is understood that such a Coulombic efficiency can also be observed for at least about 700 cycles, at least about 1,000 cycles, at least about 5,000 cycles, at least about 10,000 cycles, or at least about 20,000 cycles.

[109] In still further aspects, in the operation of any of the disclosed herein batteries, a cathode redox may or may not involve alkali metal polysulfide formation and/or shuttling.

[110] In still further aspects, the secondary batteries disclosed herein are capable of operating in a temperature range from about -30 °C to about 60 °C, including exemplary values of about -25 °C, about -20 °C, about -15 °C, about -10 °C, about -5 °C, 0 °C, about 5 °C, about 10 °C, about 15 °C, about 20 °C, about 25 °C, about 30 °C, about 35 °C, about 40 °C, about 45 °C, about 50 °C, and about 55 °C. It is further understood that the batteries can operate at any value that falls between any foregoing values on in any range that is formed by any of the disclosed values. For example, the secondary batteries disclosed herein are capable of operating in a temperature range from about -25 °C to about 60 °C, about -10 °C to about 60 °C, about 0 °C to about 60 °C, about 10 °C to about 60 °C, about 20 °C to about 60 °C, about 30 °C to about 60 °C, or about 40 °C to about 60 °C, or about -30 °C to about

50 °C, -30 °C to about 40 °C, about -30 °C to about 30 °C, about -30 °C to about 20 °C, about -30 °C to about 10 °C, about -30 °C to about 0 °C, and so on.

[111] By way of example, the secondary batteries of the present disclosure may be used in portable batteries, including those in hand-held and/or wearable electronic devices, such as a phone, watch, or laptop computer; in stationary electronic devices, such as a desktop or mainframe computer; in an electric tool, such as a power drill; in an electric or hybrid land, water, or air-based vehicle, such as a boat, submarine, bus, train, truck, car, motorcycle, moped, powered bicycle, airplane, drone, other flying vehicle, or toy versions thereof; for other toys; for energy storage, such as in storing electric power from wind, solar, wave, hydropower, or nuclear energy and/or in grid storage, or as a stationary power store for small-scale use, such as for a home, business, or hospital.

[112] In addition, according to the present disclosure, the batteries can be multi-cell batteries containing at least about 10, at least about 100, at least about 500, between 10 and 10,000, between 100 and 10,000, between 1,000 and 10,000, between 10 and 1000, between 100 and 1,000, or between 500 and 1,000 individual batteries of the present disclosure. Cells in multi-cell batteries may be arranged in parallel or in series.

METHODS

[113] Also disclosed herein are methods of making any of the disclosed above cathode materials. In certain aspects, disclosed herein is a method comprising: (a) forming a mixture comprising an alkali metal or an alkaline-earth metal, one or more transition metals, and a chalcogen-group element; (b) heating the mixture to form an active material represented by M^1M^2X , wherein M^1 is an alkali metal ion or an alkaline-earth metal ion, wherein M^2 comprises one or more transition metal ions,; and wherein X comprises at least one chalcogen anion, and wherein M^1 , M^2 , and X are present in a predetermined ratio.

[114] In still further aspects, M^1 is Li, Na, K, or a combination thereof. Yet in still further aspects, M^2 is Co, Fe, Mn, Ni, Al, B, V, Ti, Cr, Cu, Ga, Si, Ge, As, Zr, Nb, Ta, Mo, W, Pd, Pt, Re, Cd, or a combination thereof. In still further aspects, M^2 can comprise a dopant present in any of the disclosed above amounts. In yet still further

aspects, M^2 can comprise one or more of Mg, Ba, Ca, Sr, Al, B, Ga, Si, Ge, As, Zn, Sn, Sb, In, or any combination thereof.

[115] In still further aspects, X is an anion of S, Se, Te, O, or a combination thereof.

[116] In still further aspects, the active material can further comprise Y and is represented by M^1M^2XY , wherein Y comprises a halogen, and wherein M^1 , M^2 , X, and Y are present in a predetermined ratio.

[117] In some exemplary and unlimited aspects, the active material formed by the disclosed herein methods can be represented by $M_a^1M_b^2X_cY_d$, wherein M^1 is Na, $2 \leq a \leq 7$, M^2 is one of Co, Fe, Mn, Ni, V, Ti, Cr, Cu, Zr, Nb, Ta, Mo, W, Pd, Pt, Re, Cd, or a combination thereof, $0 < b \leq 2$; X is one or more of S, Se, Te, O, or a combination thereof $2 < c \leq 5$, Y is a halogen, and wherein $0 \leq d \leq 1$, where the exemplary values of x, b, c, and d are disclosed above.

[118] In still further aspects, the mixture is formed from the elemental materials. For example, and without limitations, the mixture can comprise elemental Na, elemental transition metal and elemental chalcogen, for example, sulfur. In such aspects, the active material can be formed by the direct heating of such a mixture.

[119] In certain aspects, the mixture can be formed from at least one of the alkali metals, the alkaline-earth metal, one or more transition metals, and the chalcogen-group element in the mixture is present as an ion. For example, in some aspects, at least one of the alkali metals, the alkaline-earth metal, one or more transition metals, and the chalcogen-group element in the mixture are present as an ion. In such exemplary aspects, the mixture can comprise a salt of the alkali or alkaline-earth metal and a salt of the transition metal. In certain aspects, one of the salts can comprise at least one chalcogen element. Yet, in other aspects, the mixture can comprise chalcogen anion. In yet other aspects, the mixture can comprise at least one of the alkali metal ions, the alkaline-earth metal ions, and the chalcogen element in elemental form. In certain aspects, the active material can be formed by the direct heating of such a mixture.

[120] In certain aspects, when the mixture comprises some of the disclosed constituents in ionic form, such a mixture can be formed in a first solvent. In aspects where the mixture is formed in the first solvent, the first solvent is an aqueous

solution, an organic solvent, or a combination thereof. In certain aspects, the first solvent is water. In yet other aspects, the first solvent is an organic solvent such as alcohol, N-methyl pyrrolidone, water, alcohols, acetone, toluene, acetonitrile, or a combination thereof. In still further aspects, the first solvent is a mixture of water and any of the disclosed herein organic solvents.

[121] In still further aspects, the mixture comprises some of the disclosed constituents in ionic form, such a mixture can comprise a reducing or an oxidizing agent. In certain aspects, the reductive agent is present, and it can comprise carbon, aluminum, or any combination thereof.

[122] In still further aspects, the mixture can comprise any of the disclosed above conductive agents, binders, or a combination thereof.

[123] In still further aspects, the step of heating the powder is performed at a temperature of about 500 °C to about 1000 °C, including exemplary values of about 550 °C, about 600 °C, about 650 °C, and about 700 °C, about 750 °C, about 800 °C, about 850 °C, about 900 °C, and about 950 °C in one or more heating steps. In still further aspects, the temperature can have a value that falls between any of the forgoing values or can fall within a range formed by any of the disclosed above values.

[124] In still further aspects, the method of forming the cathode electrode can further comprise forming a slurry of the active material and a binder in a second solvent. In such aspects, the binder can be any of the disclosed above binders. In still further aspects, the second solvent comprises one or more organic solvents. Any known in the art organic solvents that are suitable for battery applications can be utilized.

[125] In still further aspects, the slurry is disposed on a substrate, and the second solvent is substantially removed. In such aspects, the substrate and cathode materials are heated to dry the cathode material and remove the slurry. In still further aspects, the substrate can be any conductive material known in the art. In certain aspects, the substrate can be a powder, a film, a connector, a mesh, a foam, or any combination thereof.

[126] Also, disclosed herein is a method comprising: providing any of the disclosed herein cathode electrodes; providing any of the disclosed herein anode electrodes; providing any of the disclosed herein electrolytes; and providing any of the disclosed herein separators; forming any of the disclosed herein secondary batteries.

[127] By way of a non-limiting illustration, examples of certain aspects of the present disclosure are given below.

EXAMPLES

[128] The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how the compounds, compositions, articles, devices, and/or methods claimed herein are made and evaluated and are intended to be purely exemplary and are not intended to limit the disclosure. Efforts have been made to ensure accuracy with respect to numbers (e.g., amounts, temperature, etc.), but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight, temperature is degrees C or is at ambient temperature, and pressure is at or near atmospheric.

METHODS

[129] Preparation of $\text{Na}_6\text{CoS}_4@\text{C}$, $\text{Na}_6\text{FeS}_4@\text{C}$, $\text{Na}_6\text{MnS}_4@\text{C}$, and $\text{Na}_6\text{ZnS}_4@\text{C}$

[130] A one-pot chemical method for the preparation of carbon-coated Na_6CoS_4 ($\text{Na}_6\text{CoS}_4@\text{C}$) was developed. First, a mixture of Na_2SO_4 , $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, Ketjen Black carbon, and polyvinylpyrrolidone (average MW $\sim 1,300,000$) in certain amounts were added into an ethanol-water solution (1:1 = v: v). The obtained mixture was then intensively ultrasonicated for 30 min to form a uniform suspension. Then, the mixture was transferred to a rotary evaporator to dry the mixture and recycle the ethanol at 60 °C for several hours. The dried sample was further dry ball-milled with a planetary ball mill. The milling duration was 15 iterations of 30 minutes of milling, followed by 30 minutes of rest. Then, the fine powder obtained was heated at 800 °C for 2 h with a heating and cooling rate of 5 °C min⁻¹ to obtain $\text{Na}_6\text{CoS}_4@\text{C}$. The content of $\text{Na}_6\text{CoS}_4@\text{C}$ was determined to be ~ 90 wt.% by comparing the weight of $\text{Na}_6\text{CoS}_4@\text{C}$ before and after stirring in HCl for one day since Na_6CoS_4 is soluble in HCl. The $\text{Na}_6\text{FeS}_4@\text{C}$, Na_6MnS_4 , and Na_6ZnS_4 were prepared following

the same process as for $\text{Na}_6\text{CoS}_4@\text{C}$ except with the use of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ or $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ instead of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$.

[131] Preparation of the $\text{Na}_6\text{CoS}_4@\text{C}$ cathode. Wet milling was conducted in a PTFE bottle with a mixture of 80 wt.% composite cathode, 5 wt.% CNT, 5 wt.% super-P, and 10 wt.% PVP/PEO binder in DME/acetonitrile with a zirconia grinding medium for 24 h with a long roll jar-milling system. After coating the above slurry onto an aluminum foil, the electrode was dried inside a glove box at 60 °C for 24 h to remove the solvent. The cathodes with a Na_6CoS_4 content of 72 wt.% were obtained.

[132] Characterizations. The crystalline structures of the obtained samples were characterized by powder X-ray diffraction (PXRD) (Rigaku a MiniFlex 600 X-ray diffractometer) with $\text{Cu K}\alpha$ ($\lambda = 1.54184 \text{ \AA}$) radiation. The morphology investigation was performed with a scanning electron microscope (FEI Quanta 650 SEM) operated at 20 kV. XPS analysis was performed with a Kratos Analytical spectrometer at room temperature with monochromatic $\text{Al K}\alpha$ (1,486.6 eV) radiation. TEM and STEM analyses were performed with a JEOL 2010F field emission TEM at 200 kV.

[133] Synchrotron X-ray diffraction (XRD). Synchrotron-based operando energy dispersive X-ray diffraction (ED-XRD) measurements were conducted with beamline 6BM-A at the Advanced Photon Sources in Argonne National Laboratory. The white X-ray radiation was generated by bending magnets with an energy range of 20 – 200 keV. The detection angles were 2.477° for the Canberra germanium detector to collect the diffraction pattern. The operando experiment was conducted with a transmission geometry and provided spatial and temporal mapping capabilities. Coin cells were cycled at C/10 within 1.2 to 2.8 V, during which the ED-XRD patterns were collected for 60 s at one point. The height (10 μm) and width (2 mm) of the incident X-ray beam were kept constant during the measurement. Two points at different amplitudes, corresponding to different locations to the separator, were measured continuously until the cells went through one full cycle. The measured intensities of the two data points were added to improve the signal-to-noise ratio. Rietveld refinement was not applied to calculate the crystalline lattice parameters because of the limited detectable Q range and different X-ray energies during measurement. Instead, the peak positions of the (101) peak and (003) peak were identified and

used to calculate the evolution of the crystalline lattice parameters. It is worth noting that the accuracy of the fitted lattice parameters was affected by the broadening of these two peaks and the signal-to-noise ratio.

[134] Electrochemical measurements. Coin-type (CR2032) cells were assembled inside an Ar-filled glove box with sodium metal as the anode and Celgard 2500 separator. The monolayer dimension of the pouch cell in our work was 4.78 cm × 8.15 cm, and the cycling pressure was 35 psi. An Arbin battery cycler was used to conduct the cycling test between 1.2 and 2.8 V with a current rate of C/10, assuming a 495 mA h g⁻¹ capacity, at room temperature.

[135] Theoretical Calculations. All calculations were carried out with the standard DFT using the Vienna ab initio Simulation Package (5.4.4 VASP) within the generalized gradient approximation (GGA) as formulated by the Perdew–Burke–Ernzerhof (PBE) functional. An energy cutoff of 500 eV was adopted, and the Brillouin zone was sampled with 3×3×4 k-points using the Monkhorst-Pack scheme grid for geometry optimization and self-consistent calculations. Supercells of Na₁₂Zn₂S₈, Na₁₂Mn₂S₈, Na₁₂Co₂S₈, and Na₁₂Fe₂S₈ were selected to compare the differences in electronic structural properties. The atomic position was fully relaxed until the maximum force on each atom and total energy change was less than 0.02 eV/Å and 10⁻⁵ eV.

EXAMPLE 1

[136] In this example, a new class of ternary transition-metal sulfides (Na₆MS₄), including Na₆MnS₄, Na₆FeS₄, Na₆CoS₄, and Na₆ZnS₄, as cathodes for SIBs with high capacities is presented. These materials are known to display interesting magnetic and optical properties (10-13), but their electrochemical properties are not known. Here, a facile way to synthesize Na₆MS₄ (M = Mn, Fe, Co, and Zn) *via* a carbothermal reaction is presented. Unlike the conventional layered oxide cathodes used in LIBs and SIBs that rely exclusively on the redox of transition metals (cationic), the reversible reaction of Na₆MS₄ involves an anionic redox process. They exhibit remarkably high reversible capacities of close to 400 mAh g⁻¹ with a long cycle life, following an initial six-electron conversion reaction involving a

transformation from highly crystalline to an amorphous structure, which shows great potential compared to most published cathodes for SIBs as demonstrated in FIG. 1B.

The need for anion-redox-based materials

[137] For SIBs, there are 3 major classes of inorganic cathode materials. A schematic showing their operation mechanisms is given in FIG. 1A. The specific capacities, energy densities, and cycle life of some common SIB cathode materials are shown in FIG. 1B and are detailed in Tables 1 and 2.

Table 1. A comparative analysis of the cycling performances of Na₆CoS₄@C shown in this work, and the literature reports on other cathodes for sodium-ion batteries

Material	Rate (C)	Specific capacity (mAh g ⁻¹)	Cycle number	Cell type	Reference
Na₆CoS₄@C	0.1	392	500	coin	This work
	0.1	408	40	Anode-free	
	0.1	341	200	pouch	
Na _{1.72} MnFe(CN) ₆	1	120	30	Coin	R1
K _{0.4} [Ni _{0.2} Mn _{0.8}]O ₂	1	166.84	500	Coin	R2
Na ₃ Mn(TiO ₄) ₃	1	56.74	100	Coin	R3
Na ₃ Ni ₂ RuO ₆	1	77	1000	Coin	R4
Na ₄ MnCr(PO ₄) ₃	0.2	122.86	50	Coin	R5
Na ₃ V _{1.9} (Ca,Mg,Al,Cr,Mn) _{0.1} (PO ₄) ₂ F ₃	1	102.5	300	Coin	R6
Na _{0.67} Ni _{0.33} Mn _{0.67} O ₂	0.1	96.55	50	Coin	R7
Ca _{0.07} Na _{0.26} MnO ₂	50	24.4	1000	Coin	R8
P2-type Na _{2/3} Ni _{1/6} Mn _{2/3} Cu _{1/9} Mg _{1/18} O ₂	5	53.325	1000	Coin	R9
Na _{2/3} Li _{1/6} Fe _{1/6} Co _{1/6} Ni _{1/6} Mn _{1/3} O ₂	5	71.34	300	Coin	R10
Na _{3.75} V _{1.25} Mn _{0.75} (PO ₄) ₃	5	84.48	100	Coin	R11
NASICON Na ₃ Cr _{0.5} V _{1.5} (PO ₄) ₃	0.2	141.5	100	Coin	R12
	5	97.7	500	Coin	
Na _{0.07} NFMO ₂	1	178.2	500	Coin	R13
Na _{3.14} V _{1.93} Na _{0.07} (PO ₄) ₂ F ₃	10	75.13	1000	Coin	R14
O3-type Na(Ni _{0.3} Fe _{0.4} Mn _{0.3})O ₂	0.2	115	100	Coin	R15
Na _{0.44} MnO ₂	0.5	84.2	1000	Coin	R16
O'3-Na ₃ Ni ₂ BiO ₆	0.05	96.46	50	Coin	R17
P2-Na _{0.67} Ni _{0.33} Mn _{0.67} O ₂	0.01	89.6	10	Coin	R18
P2-Na _{0.67} Ni _{0.33} Ti _{0.67} O ₂	0.05	69.75	30	Coin	R19
P2-Na _{0.6} Cr _{0.6} Ti _{0.4} O ₂	0.1	69.56	200	Coin	R20

Material	Rate (C)	Specific capacity (mAh g ⁻¹)	Cycle number	Cell type	Reference
P2-Na _{0.67} Ni _{0.17} Co _{0.17} Ti _{0.67} O ₂	0.2	51.865	500	Coin	R21
P2-Na _{0.6} Mn _{0.8} Li _{0.2} O ₂	0.067	190	100	Coin	R22
NVP@rGO	5	92	300	Coin	R23
Na _{0.44} Mn _{0.89} Ti _{0.11} O ₂	5	71	1000	Coin	R24
C-coated Na _{3.64} Fe _{2.18} (P ₂ O ₇) ₂	2	66	1000	Coin	R25
P2-Na _{0.67} MnO ₂	10	102	500	Coin	R26
P3- Na _{2/3} Ni _{1/4} Mg _{1/12} Mn _{2/3} O ₂	0.1	108.75	50	Coin	R27
	1	97.5	100	Coin	
Spinel-layered Mn-based oxide cathode	0.1	142.9	150	Coin	R28
Na ₃ V ₂ (PO ₄) ₃ anchored on freestanding graphite foam (NVP@C-GF)	100	54	20000	Coin	R29
Na ₃ V ₂ O ₂ (PO ₄) ₂ F/graphene aerogels	1	126.49	500	Coin	R30
	5	97.9	500	Coin	
Na _{2/3} (Fe _{1/2} Mn _{1/2})O ₂ nanofibers	0.1	166	80	Coin	R31
Spongy 3D Na _{3.32} Fe _{2.34} (P ₂ O ₇) ₂ @C	5	59	1000	Coin	R32
	0.5	105.6	300	Coin	
NMZVP@cPAN	5	82	1000	Coin	R33
NaNi _{0.4} Mn _{0.25} Ti _{0.3} Co _{0.05} O ₂	0.5	98	180	Coin	R34
Na ₂ FePO ₄ F/C	4	50.82	1000	Coin	R35
O3/O'3-P2	0.1	97	200	Coin	R36
O3-Na _{0.95} Ni _{0.40} Fe _{0.15} Mn _{0.3} Ti _{0.15} O ₂	5	104.7	200	Coin	R37
P2-Na _{0.75} Ni _{1/3} Ru _{1/6} Mn _{1/2} O ₂	10	81	500	Coin	R38
Na _{0.07} Li _{0.06} Mg _{0.06} Ni _{0.22} Mn _{0.67} O ₂	0.1	85	50	Coin	R39
NVP/C	1	114	100	Coin	R40
O3-Na _{0.9} Cu _{0.22} Fe _{0.3} Mn _{0.48} O ₂	0.1	97	100	Coin	R41
NaNi _{0.6} Co _{0.05} Mn _{0.35} O ₂	0.1	131.88	100	Coin	R42
maricite NaFePO ₄	0.05	134.9	200	Coin	R43
Na ₃ V(PO ₃) ₃ N/NGO	0.1	78.9	100	Coin	R44
Na ₃ V ₂ (PO ₄) ₂ F ₃	0.091	108.9	50	Coin	R45
Na ₄ Fe ₃ (PO ₄) ₂ P ₂ O ₇	0.1	110.9	100	Coin	R46
Na _{3.1} V ₂ (PO ₄) _{2.9} (SiO ₄) _{0.1}	0.2	107.2	500	Coin	R47
Na ₂ Mn _{0.15} Co _{0.15} Ni _{0.1} Fe _{0.6} Fe(CN) ₆	0.1	94.9	500	Coin	R48
Na _{1.58} Fe[Fe(CN) ₆] _{0.92} nanosphere	0.1	127.8	800	Coin	R49
Na _{1.92} Fe ₂ (CN) ₆	0.067	125.6	1000	Coin	R50
Na ₂ RuO ₃	0.2	160.2	50	Coin	R51
Prussian Blue	1	78	1000	Coin	R52

[138] The first class of SIB cathode materials are intercalation compounds – these have a host crystal structure with channels for Na^+ ions to be inserted and extracted (FIG. 1A, left). Examples include transition-metal oxides, sulfides, polyanionic materials, and Prussian blue or white materials, wherein the active redox center is the transition-metal ion. As the host structure tends to be stable, they are rechargeable for a few hundred to a few thousand cycles. Unfortunately, the multi-atomic nature of the host structure and a redox reaction with one or less than one electron transfer per transition-metal ion translates to a low theoretical capacity – typically $< 200 \text{ mAh g}^{-1}$ and despite a high operating voltage ($> 3 \text{ V vs. Na/Na}^+$) to a low theoretical energy density of $< 600 \text{ Wh kg}^{-1}$ (FIG. 1B).

[139] The other class of inorganic cathode materials are elemental cathodes, such as sulfur and oxygen. They typically undergo conversion directly from their elemental form to their reduced form through multi-electron reactions on a lightweight substrate, such as carbon (FIG. 1A, center), and thus possess a very high capacity $> 1,000 \text{ mAh g}^{-1}$, and despite a lower voltage (between 1.5 to 3 V), they have a theoretical energy density of $> 1,500 \text{ Wh kg}^{-1}$. However, these conversion reactions are sluggish and inefficient and often involve parasitic reactions. Consequently, the cycle life is poor, typically ranging from a few tens to a couple of hundred cycles (FIG. 1B).

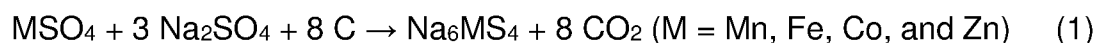
Table 2. A comparative analysis of the theoretical capacities of the cathodes in this work and the other cathodes in the literature for sodium-ion batteries.

Material	Theoretical capacity (mAh g ⁻¹)	Average Voltage (V)	Energy Density (Wh/kg)	Reference
Na₆CoS₄	495	1.87	925.6	This work
Na ₃ Ni ₂ RuO ₆	130	2.92	379.6	R1
Na ₃ V ₂ (PO ₄) ₃	110	3.4	370	R2
Na ₄ MnCr(PO ₄) ₃	160.5	3.53	556.5	R2
Na ₃ V _{1.9} (Ca,Mg,Al,Cr,Mn) _{0.1} (PO ₄) ₂ F ₃	128.3	3.47	445.5	R3
Na _{2/3} Li _{1/6} Fe _{1/6} Co _{1/6} Ni _{1/6} Mn _{1/3} O ₂	186.8	4.5	840.6	R4
NASICON Na ₃ Cr _{0.5} V _{1.5} (PO ₄) ₃	140	3.8	532	R5
Na _{0.44} MnO ₂	121	3	363	R6
NVP	117	3.4	397.8	R7
Na _{3.64} Fe _{2.18} (P ₂ O ₇) ₂	106	4	424	R8
Na _{3.32} Fe _{2.34} (P ₂ O ₇) ₂	117.4	3	352.2	R9
Na ₂ FePO ₄ F	124	4.5	558	R10
P2/P3-Na _{0.7} Li _{0.06} Mg _{0.06} Ni _{0.22} Mn _{0.67} O ₂	119	3.36	400	R11
NFM	160	3.5	560	R12
Na _{0.78} Cu _{0.27} Zn _{0.06} Mn _{0.67} O ₂	120	3.4	408	R13
Prussian white (PW)	169	3.6	608	R14
Prussian Blue (PB)	170	3.6	612	R15

[140] At the intersection of these two material classes are hybrid or anion-redox-based cathodes. These are transition-metal oxides or sulfides, but with the anions acting as the active redox species. These materials possess a host crystal structure that could undergo rearrangements to facilitate the conversion of the anions within a matrix (FIG. 1A, right). Therefore, the reactions are not sluggish and are efficient. Consequently, a life of a few hundred cycles can be obtained. As the anions undergo multi-electron reactions, capacities between 300 and 500 mAh g⁻¹ can be obtained.

Synthesis of cathode materials

[141] A facile, scalable synthesis of Na₆MS₄ is critical for its practical application in SIBs. Here, according to reaction 1, a facile carbothermal reduction of metal sulfates with carbon to obtain Na₆MS₄ was developed, as shown in Reaction (1).



[142] In Reaction (1), excess carbon was employed to ensure a complete reduction of the sulfates and ensure efficient conversion. Any unreacted, remaining carbon will also serve to construct a conductive network within the cathode. The procedure is detailed below by taking Na₆CoS₄ as an example. It is understood, however, that cathode materials with different than Na alkali metals (for example, Li or K metals)

can also be prepared. Initially, all the reactants (Ketjen Black, Na_2SO_4 , and CoSO_4) were ultrasonically mixed in water and ethanol and transferred to a rotary evaporator to dry the mixture. Followed by a high-temperature treatment of the mixture at 800 °C under nitrogen, Na_6CoS_4 was obtained. A similar procedure was adopted with $\text{M} = \text{Co}, \text{Fe}, \text{Mn}, \text{Zn}$ in Na_6MS_4 . Such a one-pot synthesis ensures a molecular-level mixing of the reactants, leading to the formation of nanosized Na_6MS_4 particles in the carbon matrix ($\text{Na}_6\text{MS}_4@\text{C}$).

[143] As shown in FIG. 2A, Na_6MS_4 crystallizes in the hexagonal $P6_3mc$ space group. The structure is comprised of a hexagonal closed-packed sulfur lattice in which the M^{2+} ions occupy the tetrahedral sites, forming MS_4 tetrahedra, while the Na^+ ions occupy both the tetrahedral and octahedral sites equally, creating two inequivalent Na^+ sites in a 1:1 ratio. In the resulting structure, the NaS_4 tetrahedra share faces, while the NaS_6 octahedra share edges with the MS_4 tetrahedra (11). The structure of $\text{Na}_6\text{MS}_4@\text{C}$ was investigated with scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in FIG. 3B and 3C, the $\text{Na}_6\text{CoS}_4@\text{C}$ composite comprises nanoparticles clustered in secondary particles of approximately 1 μm that are interconnected to form a three-dimensional porous network. The distribution of $\text{Na}_6\text{CoS}_4@\text{C}$ is further revealed by the elemental mapping images in FIGs. 3A-3F, suggesting that Na_6CoS_4 is uniformly distributed along with carbon. The XRD pattern in FIG. 4 confirms the high crystallinity of Na_6CoS_4 (PDF#86-1254). In addition, the Na_6CoS_4 was also prepared according to the previously reported method (12). As shown in FIG. 5, the prepared sample shows impurity phases, such as $\text{Na}_5\text{Co}_2\text{S}_5$ and Na_2S . These results further confirm that the method disclosed herein ensures a molecular-level mixing of the reactants, leading to a uniform reaction. All the other samples, including $\text{Na}_6\text{FeS}_4@\text{C}$, $\text{Na}_6\text{MnS}_4@\text{C}$, and $\text{Na}_6\text{ZnS}_4@\text{C}$, also show structures similar to $\text{Na}_6\text{CoS}_4@\text{C}$, as seen in FIGs. 6 - 14.

[144] As shown in FIG. 2A, amongst the transition metal ions, Co^{2+} and Fe^{2+} should be good choice for sulfides since the $\text{Co}^{2+/3+}$: 3d and $\text{Fe}^{2+/3+}$: 3d redox couples are expected to be pinned at the top of the S^{2-} : 3p band. The spin-projected density of states (pDOS) for Na_6ZnS_4 , Na_6MnS_4 , Na_6CoS_4 , and Na_6FeS_4 were calculated, and the results are plotted in FIG. 2B. The results reveal that Na_6ZnS_4 and Na_6MnS_4

have a wider bandgap compared to Na_6CoS_4 and Na_6FeS_4 due to the differences in the location of the M: 3d-band with respect to the top of the S:3p band, suggesting that both Na_6CoS_4 and Na_6FeS_4 would have better electronic conductivity

Electrochemical performances

[145] The electrochemical performances of the $\text{Na}_6\text{MS}_4@\text{C}$ samples were evaluated in Na half cells, and the voltage profiles are summarized in FIG. 2C. $\text{Na}_6\text{ZnS}_4@\text{C}$ shows inferior electrochemical activity, as only two Na^+ ions could be reversibly extracted. The redox activity in $\text{Na}_6\text{ZnS}_4@\text{C}$ is clearly due to the anion redox of S^{2-} as Zn^{2+} with a $3d^{10}$ configuration would not be expected to participate or form Zn^{3+} . Also, the limited redox activity in $\text{Na}_6\text{ZnS}_4@\text{C}$ is due to the lying of $\text{Zn}^{2+/+}$ energy well above the top of the S^{2-} : 2p band and lack of covalent mixing between Zn: 3d and S: 2p orbitals (FIGs. 2B-2C). This contrasts with $\text{Na}_6\text{CoS}_4@\text{C}$ and $\text{Na}_6\text{FeS}_4@\text{C}$ (FIG. 2C), which have much larger electrochemical activity due to the high covalence of the M-S bond, resulting from a significant overlap of the $\text{M}^{2+/3+}$: 3d band with the top of the S^{2-} : 2p band (FIG. 2A).

[146] The cycling performances of $\text{Na}_6\text{ZnS}_4@\text{C}$, $\text{Na}_6\text{MnS}_4@\text{C}$, $\text{Na}_6\text{CoS}_4@\text{C}$, and $\text{Na}_6\text{FeS}_4@\text{C}$ are shown in FIG. 15A. It was found that under certain conditions, $\text{Na}_6\text{ZnS}_4@\text{C}$ and $\text{Na}_6\text{MnS}_4@\text{C}$ cathodes show large irreversible capacities that can fade below 50 mAh g^{-1} after 5 cycles due to the lack of covalence. In contrast, $\text{Na}_6\text{CoS}_4@\text{C}$ and $\text{Na}_6\text{FeS}_4@\text{C}$ show good reversible cycling performance. In this example, $\text{Na}_6\text{CoS}_4@\text{C}$ was selected as a model system to further demonstrate the potential of ternary transition-metal sulfides. The $\text{Na}_6\text{CoS}_4@\text{C}$ cathode delivers a high initial charge-specific capacity of 477 mAh g^{-1} at 0.1C rate, which corresponds to $\sim 5.8 \text{ Na}^+$ ions extracted from $\text{Na}_6\text{CoS}_4@\text{C}$. Then, 5.3 Na^+ ions could be inserted reversibly, which corresponds to a discharge capacity of 437 mAh g^{-1} . The discharge capacity becomes stable at 392 mAh g^{-1} in the subsequent cycles. The fast decay in the first two cycles is mainly due to the transformation of highly crystalline Na_6CoS_4 to an amorphous structure and cathode-electrolyte interphase (CEI) formation, which will be further discussed later. Even after 500 cycles, $\text{Na}_6\text{CoS}_4@\text{C}$ maintains a capacity of 306 mAh g^{-1} , corresponding to a capacity fade rate of 0.04% per cycle. Also, $\text{Na}_6\text{CoS}_4@\text{C}$ exhibits an average Coulombic efficiency of 99.6% over 500 cycles at a 0.1C rate, indicating high reversibility of the conversion and good

structural integrity during repeated cycling. FIG. 16 shows the cyclic voltammetry (CV) curves of the $\text{Na}_6\text{CoS}_4@\text{C}$ cathode for the first six cycles in the voltage range of 1.2 to 2.8 V with a scanning rate of 0.1 mV s^{-1} . A strong anodic peak at 2.27 V was detected in the initial scanning, which can be attributed to the transformation of the crystalline Na_6CoS_4 to an amorphous structure and finally to S/CoS. The cathodic peak at 1.52 V is associated with the conversion of S/CoS back to Na_6CoS_4 . After the first sweep, the overlapping CV curves indicate a good reversibility of the conversion.

[147] FIG. 15B shows the charge/discharge profiles of the $\text{Na}_6\text{CoS}_4@\text{C}$ cathode at 0.1C rate. The voltage plateaus match well with the CV results in FIG. 16. Only a slight change in the potential plateau, even after 500 cycles, confirms the high-capacity reversibility of the $\text{Na}_6\text{CoS}_4@\text{C}$ cathode. As shown in FIG. 17C, the rate capability of $\text{Na}_6\text{CoS}_4@\text{C}$ was conducted at various C rates. $\text{Na}_6\text{CoS}_4@\text{C}$ exhibits excellent rate capability with high reversible specific capacities of 418, 354, 312, 283, 240, 197, and 156 mAh g^{-1} at, respectively, 0.1 C, 0.2 C, 0.5 C, 1 C, 1.5 C, 2 C, and 4 C rates. Notably, the capacity recovers to 386 mAh g^{-1} as the C rate is reduced from 4C to 0.1C, indicating the stability of the $\text{Na}_6\text{CoS}_4@\text{C}$ cathode at high rates.

[148] The $\text{Na}_6\text{CoS}_4@\text{C}$ cathode was further evaluated under a high active material (AM) loading of 5 mg cm^{-2} and a low electrolyte/AM ratio of $7 \text{ } \mu\text{L mg}^{-1}$ to demonstrate the practical viability of Na_6CoS_4 . As shown in FIG. 15D, the cell with a high Na_6CoS_4 loading and a low electrolyte amount practically maintains a cycling performance similar to the cell with a low Na_6CoS_4 loading, demonstrating the outstanding redox kinetics of the Na_6CoS_4 .

[149] As shown in FIG. 15E, the pouch cell with a $\text{Na}_6\text{CoS}_4@\text{C}$ loading of 2 mg cm^{-2} and a low electrolyte/AM ratio of $7 \text{ } \mu\text{L mg}^{-1}$ delivers an initial specific capacity of 341 mAh g^{-1} . Even after 200 cycles, the pouch cell maintains a high specific capacity of 293 mAh g^{-1} , the most extended cycling lifespan of sodium-ion pouch cells, as summarized in Table 1. It should be noted that after the initial 10 cycles, the pouch cell shows almost no capacity decay upon cycling. To further pursue the practical viability of $\text{Na}_6\text{CoS}_4@\text{C}$ cathode in pouch cell, the loading was further improved to 5.3 mg cm^{-2} , and the electrolyte amount was further reduced to $4 \text{ } \mu\text{L mg}^{-1}$. As shown in FIG. 15F, the pouch cell with a high loading can deliver a high initial capacity of

357 mAh g⁻¹ and remain stable over 60 cycles. The results further illustrate the stability of the Na₆CoS₄@C cathode.

[150] To further demonstrate the advantage of using the sodium-containing Na₆CoS₄@C cathode, an anode-free cell was constructed with a localized high-concentration electrolyte (LHCE) and Ni foil as the anode current collector for Na deposition. As shown in FIG. 15G, the Ni||Na₆CoS₄@C cell can still deliver an initial discharge capacity of 408 mAh g⁻¹, which is very close to that of the Na||Na₆CoS₄@C cell paired with a Na-foil anode, suggesting an efficient deposition of Na in an anode-free Ni||Na₆CoS₄@C cell. The Ni||Na₆CoS₄@C anode-free cell maintains 187 mAh g⁻¹ over 40 cycles, demonstrating a highly reversible reaction of Na₆CoS₄ with a high utilization of Na in the anode-free Ni||Na₆CoS₄@C cell.

Anionic redox mechanisms of Na₆CoS₄

[151] The voltage profiles in FIG. 2D indicate a significant potential difference between the first de-sodiation step (charge) and the first sodiation step (discharge) of the Na₆MS₄ class of materials. No change in the shape of the charge/discharge curve is observed in the subsequent cycles (FIG. 15B). This suggests crystalline rearrangements in Na₆MS₄ during the first cycle. This phenomenon was further investigated using a suite of *in-situ* and *in-operando* techniques, such as synchrotron-based operando energy dispersive X-ray diffraction (ED-XRD) and Raman spectroscopy with Na₆CoS₄@C cathode as the prototypical compound as it appears to be the most electrochemically reversible sample. ED-XRD was used as the ultrahigh-energy of the X-ray (up to 200 keV) at the sector 6BM-A of the Advanced Photo Source in Argonne National Laboratory, providing a deep penetration depth, allowing for identifying the structural changes in the cathode using normal coin cells (CR2032) for the measurement (14). As shown in FIG. 17A, the cell was tested at 0.1C rate (1C = 495 mA g⁻¹) between 1.2 and 2.8 V (vs. Na⁺/Na) for one full discharge-charge cycle. In the meantime, the XRD signal was recorded, as demonstrated in the contour plot (FIG. 17B) next to the charge-discharge profile. In-situ Raman spectroscopy was performed to gain an understanding of the transformations after the amorphization of Na₆CoS₄. As shown in FIG. 17C, the cell was tested at 0.1 mV s⁻¹ in the range of 1.2 to 2.8 V (vs. Na⁺/Na) for two cycles. FIG.

17D shows the time-resolved Raman image recorded on the cathode material during cycling.

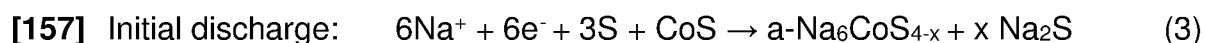
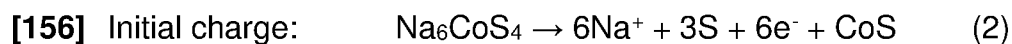
[152] In addition to in-situ techniques, *ex-situ* analysis, such as TEM and X-ray photoelectron spectroscopy (XPS), of Na_6CoS_4 at different states of cycling was conducted to investigate the detailed product phase. As described earlier, based on the covalent nature of the Co-S bonds owing to the overlap of the Co 3d band with the S 2p bands, the removal of electrons/sodium from the structure would result in an oxidation of the sulfide anions. In the contour plot of the ED-XRD data in FIG. 17B, a set of dominant peaks of Na_6CoS_4 (PDF#86-1254) with strong intensity can be observed at the initial stage of the charge process. As the charge step proceeds, the diffraction peak intensity tends to weaken. The first peak of losing detectable intensity corresponds to the (301) plane of Na_6CoS_4 , suggesting the desodiation begins with the removal of sodium from the NaS_4 tetrahedra. The next peak to lose intensity belongs to the (220) plane, indicating sodium removal from the octahedral site. At about 80% depth-of-charge, all the peaks of Na_6CoS_4 , except the ones for (101) and (211) planes, completely vanish, suggesting the transformation of the MS_4 tetrahedral unit to MS_6 octahedra, which is prevalent in CoS.

[153] This loss of intensity is corroborated by the TEM images (FIG. 18), wherein the size of the primary Na_6CoS_4 particles (FIG. 18A) changed from several 100 nm size grains to 4-8 nm size grains (FIG. 18B-D). Additionally, TEM also shows 2 – 4 nm size domains of CoS and S wrapped in the carbon matrix, confirming the observation of CoS in ED-XRD. XPS was used to track the oxidation state changes through this process. The S 2p spectrum (FIG. 18F) of the fresh sample shows two sulfur contributions at 159.8 and 162.4 eV, corresponding to, respectively, the Na-S bonds and Co-S bonds. When the $\text{Na}_6\text{CoS}_4\text{@C}$ was fully charged, the peaks in the S 2p spectrum showed a positive shift with two sulfur contributions at 162.5 and 164.1 eV, attributed, respectively, to the Co-S bonds and S-S bonds; this indicates the formation of sulfur and CoS as seen in the TEM and validates that the sulfide anions are oxidized to sulfur through anion redox. This also implies that there is little change in the oxidation state of Co. As shown in Fig. 19, the fresh $\text{Na}_6\text{CoS}_4\text{@C}$ sample shows two Co 2p_{3/2} components at 779.5 and 782.9 eV, corresponding, respectively, to Co^{2+} and Co^{2+} satellites. After fully charging, only Co^{2+} and Co^{2+}

satellites are observed, albeit with a positive shift of 0.5 eV, owing to the formation of CoS and its subsequent interaction with S.

[154] The discharge starts with the cathode having nanometer-sized domains of CoS and S. For this reason, it is hard to see any peaks in the ED-XRD. To resolve this issue, in-situ Raman spectroscopy, wherein the pristine Na₆CoS₄ can be seen in the 1,200 to 1,650 cm⁻¹ range, was used. While no peaks are observed in the charged state, during the reduction process, the intensity of the typical peaks of Na₆CoS₄ gradually becomes stronger. In addition, the peaks of Na₆CoS₄ become both broad and intense in the second cycle, suggesting the loss of long-range translational symmetry and implying the formation of nanosized Na₆CoS₄. TEM of the discharged cathode sheds light on both the morphology and identity of the cathode in the discharged state. The discharged cathode (FIG. 17E) contains a mosaic of 8 – 10 nm size grains of Na₂S and Na₆CoS₄ (Fig. 20). The elemental mapping images of the fresh and fully discharged samples in Fig. 21 and Fig. 22 suggest that Na and S along with Co are present. However, the presence of Na₂S and the broadening of peaks in the Raman spectra suggest that a small portion of the sulfur may be segregated during the first charge step, which converts back to Na₂S, while the sulfur close to CoS can become amorphous Na₆CoS_{4-x} (a-Na₆CoS₄). The loss of sulfur from the parent Na₆CoS₄ during the first cycle to yield Na₂S and the sulfur-deficient a-Na₆CoS₄ is also corroborated by the XPS data of the discharged cathode (Figure 5f), showing a higher intensity for the Na-S peaks compared to Co-S, while the Co oxidation state remains 2+ (Fig. 19). The formation of Na₂S and a-Na₆CoS₄ explains the differences in the voltage curve and the loss of some reversible capacity between the first and the second cycle.

[155] Based on the evidence from the different materials characterization techniques, we deem the unique Na₆CoS₄ reaction pathway as described below:



[159] This reaction pathway has been schematically represented in FIG. 23. The class of Na₆CoS₄ displays a six-electron redox reaction. During the initial charge

process, Na_6CoS_4 first transforms from a highly crystalline to an amorphous structure, mainly consisting of nanosized CoS and sulfur nanoparticles. Afterward, the conversion is highly reversible from amorphous a-CoS/S to a- $\text{Na}_6\text{CoS}_{4-x}$ and some Na_2S particles with rich, small, disordered crystal domains.

[160] This anion-redox-based conversion reaction possesses several advantages. First, unlike conventional sodium-sulfur batteries, the Na_6CoS_4 cathode redox does not involve sodium polysulfide (NaPSs) formation and shuttling, overcoming the capacity decay challenges of conventional sulfur cathodes. Such a conclusion can be easily confirmed by the good cycling performance of $\text{Na}_6\text{CoS}_4@\text{C}$ cathode in the conventional low-concentration electrolyte of 1 M NaFSI in DME, as shown in FIG. 24, compared to the few cycles lifespan observed in the literature for sulfur cathode in low-concentration electrolytes (15 - 17). Second, conductivity changes in the material through cycling were traced through the evolution of pDOS during the desodiation process, as shown in FIG. 25. Following the Na removal, there was a depletion of the Co 3d band and the S 3p band near the Fermi level, indicating the co-oxidation of both Co^{2+} and S^{2-} during charge, resulting from the overlap of the $\text{Co}^{2+/3+}$ and S^{2-} : 2p bands and the strong hybridization and pinning of the Co: 3d and S: 2p orbitals. We also found that the conductivity of $\text{Na}_{6-x}\text{CoS}_4$ becomes better during the Na extraction process due to the introduction of holes into the S^{2-} :3p band, which is beneficial for electrode performance.

[161] In summary, for the first time, a class of Na_6MS_4 ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{and Zn}$) is shown to serve as cathode materials for Na-ion batteries. By selecting Na_6CoS_4 as a model system, a unique cathode chemistry was discovered. During the initial charge process, Na_6CoS_4 first transforms from a highly crystalline to an amorphous structure, mainly consisting of nanosized CoS and sulfur nanoparticles. Afterward, the conversion is highly reversible from amorphous a-CoS/S to a- Na_6CoS_4 particles with rich, small, disordered crystal domains. The six-electron redox reaction was realized through such a unique conversion pathway, whose theoretical capacity is 495 mAh g^{-1} . Finally, when we compare the theoretical energy of different classes of Na-cathodes, including polyanion, layered oxide, and Prussian blue analogs, as summarized in Table 2, the $\text{Na}_6\text{MS}_4@\text{C}$ cathode family delivers the energy density of 926 Wh kg^{-1} .

EXAMPLE 2

[162] Na_6CoS_4 was prepared similarly to Example 1. The obtained Na_6CoS_4 , acetylene black, and polyvinylpyrrolidone are ground evenly in a mortar with a mass ratio of R ($R = 40:4:1$) and then transferred to a 10 ml beaker, then an appropriate amount of acetonitrile is added, and stirring is performed to obtain a slurry.

[163] The above-mentioned slurry is evenly applied on a substrate (the substrate is aluminum foil or carbon cloth), which is cut into discs with a diameter of 1.0 centimeters after vacuum drying to obtain the positive electrode plates.

[164] 2032 button batteries were prepared, and cycle testing was performed on Na_6CoS_4 prepared by the present invention.

[165] The specific assembling steps were packaging a Na_6CoS_4 positive electrode plate, a separator, and a sodium sheet in a button battery shell and performing cycle testing. The electrolyte is NaFSI:DME:TTE (1:1.2:1) electrolyte.

[166] As shown in FIG. 26, a battery having Na_6CoS_4 as the positive electrode and the sodium sheet as the negative electrode exhibited an excellent cycle performance of more than 500 cycles under a current density of 0.2A/g.

[167] Additional 2032 button batteries were prepared, and rate testing was performed on the Na_6CoS_4 prepared by the present invention. The specific assembling steps included packaging a Na_6CoS_4 positive electrode plate, a separator, and a sodium sheet in a button battery shell and performing cycle testing. The electrolyte is NaFSI:DME:TTE (1:1.2:1) electrolyte.

[168] As shown in FIG. 27, the Na_6CoS_4 positive electrode material exhibited good capacity retention and a low charging and discharging voltage platform in the cycle process.

[169] As shown in a previously presented FIG. 17A, the charging and discharging curve has both a platform and a slope, the platform represents the oxidation-reduction reaction, the slope represents the deintercalation reaction mechanism, and the reaction involved by Na_6CoS_4 is a deintercalation-redox composite reaction system.

EXAMPLE 3

[170] In this example, Na_6FeS_4 was used as a cathode electrode material.

[171] As shown in previously presented FIG 8, the X-ray diffraction pattern of Na_6FeS_4 , the upper peak is an experimental group, the lower peak is a comparison group, and it can be found that a material prepared by experiments corresponds to a standard material in peak position, indicating that the material is successfully prepared.

[172] The obtained Na_6FeS_4 , acetylene black, and polyvinylpyrrolidone are ground evenly in a mortar with a mass ratio of R (R = 40:4:1) and then transferred to a 10 ml beaker, then an appropriate amount of acetonitrile is added, and stirring is performed to obtain a slurry. The above-mentioned slurry is evenly applied on the substrate, which is cut into discs with a diameter of 1.0 centimeter after vacuum drying to obtain the positive electrode plates.

[173] 2032 button batteries were prepared, and cycle testing was performed on Na_6FeS_4 prepared by the present invention. The specific assembling steps included packaging a Na_6FeS_4 positive electrode plate, a separator and a sodium sheet in a button battery shell and performing cycle testing. Among them, the electrolyte is a NaFSI:DME:TTE (1:1.2:1) electrolyte.

[174] As shown in FIG. 28, a battery with Na_6FeS_4 as the positive electrode and the sodium sheet as the negative electrode exhibited excellent cycle performance of more than 500 cycles under a current density of 0.2A/g.

[175] 2032 button batteries were prepared, and rate testing was performed on the Na_6FeS_4 prepared by the present invention. The specific assembling steps are packaging a Na_6FeS_4 positive electrode plate, a separator and a sodium sheet in a button battery shell and performing cycle testing. The electrolyte is NaFSI:DME:TTE (1:1.2:1) electrolyte.

[176] As shown in FIG. 29, it is shown in the figure that: the Na_6FeS_4 positive electrode material has good capacity retention and a low charging and discharging voltage platform in the cycle process.

COMPARATIVE EXAMPLE

[177] Here, an NFM ($\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$) was used as a comparative cathode electrode.

[178] The obtained NFM ($\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$, classic sodium-ion positive electrode material), acetylene black, and polyvinylidene fluoride are ground evenly in a mortar with a mass ratio of R and then transferred into a 10 ml beaker, then an appropriate amount of N-methylpyrrolidone is added, and stirring is performed to form a slurry.

[179] The above-mentioned slurry is evenly coated on the substrate (aluminum foil, carbon cloth), which is cut into discs with a diameter of 1.0 centimeter after vacuum drying to obtain the positive electrode plates.

[180] 2032 button batteries were prepared, and cycle testing was performed on NFM. The specific assembling steps included packaging an NFM positive electrode plate, a separator and a sodium sheet in a button battery shell and performing cycle testing. The electrolyte is NaFSI:DME:TTE (1:1.2:1) electrolyte.

[181] As shown in FIG. 30, a battery with NFM as the positive electrode and the sodium sheet as the negative electrode has a low capacity and a cycle number smaller than 100 under a current density of 0.2A/g.

[182] Additional 2032 button batteries were prepared, and rate testing was performed on the NFM prepared by the present invention. The specific assembling steps included packaging an NFM positive electrode plate, a separator and a sodium sheet in a button battery shell and performing cycle testing. The electrolyte is NaFSI:DME:TTE (1:1.2:1) electrolyte.

[183] [As shown in FIG. 31, the NFM positive electrode material has a high voltage platform and a low-capacity retention rate in the cycle process.

[184] Table 3 is obtained through Examples 2 and 3 and Comparative Example. It can be seen that the positive electrode material of the patent invention achieves at least a nearly 3-fold increase in the first-cycle discharging capacity of the sodium battery, and the cycle stability and the capacity retention rate are greatly improved:

Table 3

	First-cycle discharging capacity (mAh g ⁻¹)	Cycle number	Capacity retention rate
Example 2	487	500	73%
Example 3	344	500	76%
Comparative Example	125	100	40%

[185] The devices, systems, and methods of the appended claims are not limited in scope by the specific devices, systems, and methods described herein, which are intended as illustrations of a few aspects of the claims. Any devices, systems, and functionally equivalent methods are intended to fall within the scope of the claims. Various modifications of the devices, systems, and methods, in addition to those shown and described herein, are intended to fall within the scope of the appended claims. Further, while only certain representative devices, systems, and method steps disclosed herein are specifically described, other combinations of the devices, systems, and method steps are also intended to fall within the scope of the appended claims, even if not specifically recited. Thus, a combination of steps, elements, components, or constituents may be explicitly mentioned herein or less; however, other combinations of steps, elements, components, and constituents are included, even though not explicitly stated.

[186] Although several embodiments of the invention have been disclosed in the foregoing specification, it is understood by those skilled in the art that many modifications and other embodiments of the invention will come to mind to which the invention pertains, having the benefit of the teaching presented in the foregoing description and associated drawings. It is thus understood that the invention is not limited to the specific embodiments disclosed hereinabove and that many modifications and other embodiments are intended to be included within the scope of the appended claims. Moreover, although specific terms are employed herein, as well as in the claims which follow, they are used only in a generic and descriptive sense and not for the purposes of limiting the described invention or the claims which follow.

[187] Unless defined otherwise, all technical and scientific terms used herein have the same meanings as commonly understood by one of skill in the art to which the disclosed invention belongs. Publications cited herein and the materials for which they are cited are specifically incorporated by reference.

[188] The claims are not intended to include, and should not be interpreted to include, means-plus- or step-plus-function limitations unless such a limitation is explicitly recited in a given claim using the phrase(s) “means for” or “step for,” respectively.

[189] In view of the described processes and compositions, herein below are described certain more particularly described aspects of the inventions. These particularly recited aspects should not, however, be interpreted to have any limiting effect on any different claims containing different or more general teachings described herein or that the “particular” aspects are somehow limited in some way other than the inherent meanings of the language and formulas literally used therein.

EXEMPLARY ASPECTS

[190] In view of the described processes and compositions, herein below are described certain more particularly described aspects of the disclosures. These particularly recited aspects should not, however, be interpreted to have any limiting effect on any different claims containing different or more general teachings described herein, or that the “particular” aspects are somehow limited in some way other than the inherent meanings of the language and formulas literally used therein.

[191] Example 1. A cathode electrode for a reversible battery comprising an active material comprising an alkali metal ion or alkaline-earth metal ion and at least one or more transition metal chalcogenides, and wherein active redox species comprise anions.

[192] Example 2. The cathode electrode of any one of the examples herein, particularly Example 1, wherein the anion redox species comprise chalcogen anion.

[193] Example 3. The cathode electrode of any one of the examples herein, particularly Examples 1-2, wherein the active material is crystalline.

[194] Example 4. The cathode electrode of any one of the examples herein, particularly Examples 1-3, wherein the active material is represented by M^1M^2X , wherein M^1 comprises Li, Na, K, or a combination thereof; wherein M^2 comprises at least one transition metal ion comprising Co, Fe, Mn, Ni, V, Ti, Cr, Cu, Zr, Nb, Ta, Mo, W, Pd, Pt, Re, Cd, or a combination thereof; wherein X comprises S, Se, Te, O, or a combination thereof; and wherein M^1 , M^2 , and X are present in a predetermined ratio.

[195] Example 5. The cathode electrode of any one of the examples herein, particularly Example 4, wherein the active material further comprises Y and is represented by M^1M^2XY , wherein Y comprises a halogen, and wherein M^1 , M^2 , X, and Y are present in a predetermined ratio.

[196] Example 6. The cathode electrode of any one of the examples herein, particularly Examples 1-5, wherein the active material further comprises a dopant.

[197] Example 7. The cathode electrode of any one of the examples herein, particularly Examples 4-6, wherein the M^2 further comprises a dopant comprising one or more of Mg, Ba, Ca, Sr, Al, B, Ga, Si, Ge, As, Zn, Sn, Sb, In, or any combination thereof.

[198] Example 8. The cathode electrode of any one of the examples herein, particularly Examples 1-7, wherein the active material is represented by $M_a^1M_b^2X_cY_d$, wherein M^1 is Na, wherein $2 \leq a \leq 7$, M^2 is one of Co, Fe, Mn, Ni, V, Ti, Cr, Cu, Zr, Nb, Ta, Mo, W, Pd, Pt, Re, Cd, or a combination thereof, wherein $0 < b \leq 2$; X is one or more of S, Se, Te, O, or a combination thereof, wherein $2 < c \leq 5$, and Y is a halogen, wherein $0 \leq d \leq 1$.

[199] Example 9. The cathode electrode of any one of the examples herein, particularly Example 8, wherein the M^2 further comprises one or more of Mg, Ba, Ca, Sr, Al, B, Ga, Si, Ge, As, Zn, Sn, Sb, In, or any combination thereof.

[200] Example 10. The cathode electrode of any one of the examples herein, particularly Example 8 or 9, wherein the M^2 is Co, Fe, Mn, or a combination thereof.

[201] Example 11. The cathode electrode of any one of the examples herein, particularly Examples 8-10, wherein X is S or Se or Te, O, or a combination thereof.

[202] Example 12. The cathode electrode of any one of the examples herein, particularly Examples 8-11, wherein when $d > 0$, Y is Cl, Br, I, F, or a combination thereof.

[203] Example 13. The cathode electrode of any one of the examples herein, particularly Examples 1-12, wherein the active material comprises Na_6CoS_4 .

[204] Example 14. The cathode electrode of v Examples 1-13, wherein the active material comprises Na_6FeS_4 .

[205] Example 15. The cathode electrode of any one of the examples herein, particularly Examples 1-14, wherein the active material further comprises a conductive agent.

[206] Example 16. The cathode electrode of any one of the examples herein, particularly Example 15, wherein the conductive agent comprises one or more of carbon black, carbon nanotubes, graphene, graphite, modified and unmodified carbon, conductive polymers, conductive oxides, conductive ceramics, or any combination thereof.

[207] Example 17. The cathode electrode of any one of the examples herein, particularly Examples 1-16, wherein the active material further comprises a binder.

[208] Example 18. A secondary battery comprising the cathode electrode of any one of the examples herein, particularly Examples 1-17.

[209] Example 19. The secondary battery of any one of the examples herein, particularly Example 18, wherein the battery further comprises an anode electrode and an electrolyte.

[210] Example 20. The secondary battery of any one of the examples herein, particularly Example 19, wherein the electrolyte is a liquid electrolyte comprising a salt and a solvent.

[211] Example 21. The secondary battery of any one of the examples herein, particularly Example 20, wherein the salt comprises a cation that is a cation of alkali and/or alkaline-earth metal present in the active material.

[212] Example 22. The secondary battery of any one of the examples herein, particularly Example 20 or 21, wherein the salt comprises one or more of sodium

fluorophosphate (NaPF_6), sodium fluoroborate (NaBF_4), sodium tetraphenylborate (NaBPh_4), sodium bis(fluorosulfonyl)imide (NaFSI), sodium bis(trifluoromethanesulfonyl)imide (NaTFSI), sodium (fluorosulfonyl)(trifluoromethanesulfonyl)imide (NaFTFSI), sodium perchlorate (NaClO_4), sodium nitrate (NaNO_3), sodium 4,5-dicyano-2-(trifluoromethyl)imidazole (NaTDI), sodium 4,5-dicyano-2-(pentafluoromethyl)imidazole (NaPDI), and sodium difluorooxalato borate (NaDFOB), or any combination thereof.

[213] Example 23. The secondary battery of any one of the examples herein, particularly Examples 20-22, wherein the solvent comprises one or more of ethylene carbonate (EC), 1,2-Dimethoxyethane (DME), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), 1,2-Dimethoxyethane (DME), fluoroethylene carbonate (FEC), tetrahydrofuran (THF), diethylene glycol dimethyl ether (Diglyme), triethylene glycol dimethyl ether (TDEM), tetraethylene glycol dimethyl ether (TEGDME), and vinylene carbonate (VC), Bis(2,2,2-trifluoroethyl) ether (BTFE), 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropylether (TTE), tris(2,2,2-trifluoroethyl) orthoformate (TFEO), trimethylphosphate (TMP), triethylphosphate (TEP), or any combination hereof.

[214] Example 24. The secondary battery of any one of the examples herein, particularly Examples 20-23, wherein the salt is present in an amount of about 0.01 M to about 3 M.

[215] Example 25. The secondary battery of any one of the examples herein, particularly Example 19, wherein the electrolyte is a solid electrolyte.

[216] Example 26. The secondary battery of any one of the examples herein, particularly Examples 20-25, wherein the anode electrode comprises one or more metallic alkali and/or alkaline earth foils, alkali and/or alkaline earth powder, alkali and/or alkaline earth meshes, alkali and/or alkaline earth alloys, carbon materials, non-alkali and/or non-alkaline earth metal alloys, nonmetal alloys, compound materials, or any combination thereof.

[217] Example 27. The secondary battery of any one of the examples herein, particularly Examples 19-26, wherein the anode electrode is a current collector for an alkali metal deposition during a plating step

[218] Example 28. The secondary battery of any one of the examples herein, particularly Examples 18-27, wherein the alkali metal is sodium such that the secondary battery is a sodium-ion battery.

[219] Example 29. The secondary battery of any one of the examples herein, particularly Example 28, wherein the anode electrode comprises an elemental or compound anode suitable for sodium-ion batteries.

[220] Example 30. The secondary battery of any one of the examples herein, particularly Examples 18-29, wherein the secondary battery exhibits a specific capacity of about 100 mAh g⁻¹ to about 600 mAh g⁻¹ at a discharge rate of at least about 0.1C.

[221] Example 31. The secondary battery of any one of the examples herein, particularly Example 30, wherein the secondary battery exhibits a capacity retention of at least about 75% over at least about 200 cycles.

[222] Example 32. The secondary battery of any one of the examples herein, particularly Examples 30-31, wherein the secondary battery exhibits a capacity retention of at least about 75% over at least about 500 cycles.

[223] Example 33. The secondary battery of any one of the examples herein, particularly Examples 18-32, wherein the secondary battery exhibits coulombic efficiency of greater than about 95%.

[224] Example 34. The secondary battery of any one of the examples herein, particularly Examples 18-33, wherein a cathode redox does not involve alkali metal polysulfide formation and/or shuttling.

[225] Example 35. The secondary battery of any one of the examples herein, particularly Examples 18-34, wherein the battery is capable of operating in a temperature range of about -30 °C to about 60 °C.

[226] Example 36. A method of making a cathode electrode of any one of the examples herein, particularly Examples 1-17, wherein the method comprises: (a) forming a mixture comprising an alkali metal or an alkaline-earth metal, one or more transition metals, and a chalcogen-group element; (b) heating the mixture to form an active material represented by M¹M²X, wherein M¹ is an alkali metal ion or an alkali-

earth metal ion, wherein M^2 comprises one or more transition metal ions, and wherein X comprises at least one chalcogen anion, and wherein M^1 , M^2 , and X are present in a predetermined ratio.

[227] Example 37. The method of any one of the examples herein, particularly Example 36, wherein M^1 is Li, Na, K, or a combination thereof.

[228] Example 38. The method of any one of the examples herein, particularly Example 36 or 37, wherein M^2 is Co, Fe, Mn, Ni, Al, B, V, Ti, Cr, Cu, Ga, Si, Ge, As, Zr, Nb, Ta, Mo, W, Pd, Pt, Re, Cd, or a combination thereof.

[229] Example 39. The method of any one of the examples herein, particularly Examples 36-38, wherein X is an anion of S, Se, Te, O, or a combination thereof.

[230] Example 40. The method of any one of the examples herein, particularly Examples 36-39, wherein the M^2 further comprises one or more of Mg, Ba, Ca, Sr, Al, B, Ga, Si, Ge, As, Zn, Sn, Sb, In or any combination thereof.

[231] Example 41. The method of any one of the examples herein, particularly Examples 36-40, wherein the active material further comprises Y and is represented by M^1M^2XY , wherein Y comprises a halogen, and wherein M^1 , M^2 , X, and Y are present in a predetermined ratio.

[232] Example 42. The method of any one of the examples herein, particularly Example 41, wherein the active material is represented by $M_a^1M_b^2X_cY_d$, wherein M^1 is Na, wherein $2 \leq a \leq 7$, M^2 is one of Co, Fe, Mn, Ni, V, Ti, Cr, Cu, Zr, Nb, Ta, Mo, W, Pd, Pt, Re, Cd, or a combination thereof, wherein $0 < b \leq 2$; X is one or more of S, Se, Te, O, or a combination thereof, wherein $2 < c \leq 5$, and Y is a halogen, wherein $0 \leq d \leq 1$.

[233] Example 43. The method of any one of the examples herein, particularly Examples 36-42, wherein at least one of the alkali metal, the alkaline-earth metal, the one or more transition metals, and the chalcogen-group element in the mixture are present as an ion.

[234] Example 44. The method of any one of the examples herein, particularly Examples 36-42, wherein at least one of the alkali metal, the alkaline-earth metal,

the one or more transition metals, and the chalcogen-group element in the mixture are present in zero valence.

[235] Example 45. The method of any one of the examples herein, particularly Examples 36-43, wherein the mixture is formed in a first solvent.

[236] Example 46. The method of any one of the examples herein, particularly Example 45, wherein the first solvent is an aqueous solution, an organic solvent, or a combination thereof.

[237] Example 47. The method of any one of the examples herein, particularly Examples 36-46, wherein the mixture further comprises a reducing or an oxidizing agent.

[238] Example 48. The method of any one of the examples herein, particularly Examples 36-47, wherein the mixture comprises a reducing agent comprising carbon.

[239] Example 49. The method of any one of the examples herein, particularly Examples 36-48, wherein the mixture further comprises a conductive agent, a binder, or a combination thereof.

[240] Example 50. The method of any one of the examples herein, particularly Examples 36-49, wherein the heating of the mixture performed at a temperature of 500 °C - 1000 °C in one or more heating steps.

[241] Example 51. The method of any one of the examples herein, particularly Examples 36-50, further comprising forming a slurry of the active material and a binder in a second solvent.

[242] Example 52. The method of any one of the examples herein, particularly Example 51, wherein the second solvent comprises one or more organic solvents.

[243] Example 53. The method of any one of the examples herein, particularly Example 51 or 52, wherein the slurry is disposed on a substrate and the second solvent is substantially removed.

[244] Example 54. A method comprising: providing the cathode electrode of any one of the examples herein, particularly Examples 1-17; providing an anode

electrode; providing an electrolyte; and providing a separator; forming the secondary battery of any one of the examples herein, particularly Examples 18-35.

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CLAIMS

1. A cathode electrode for a reversible battery comprising an active material comprising an alkali metal ion or alkaline-earth metal ion and at least one or more transition metal chalcogenides, and wherein active redox species comprise anions.
2. The cathode electrode of claim 1, wherein the anion redox species comprise chalcogen anion.
3. The cathode electrode of any one of claims 1-2, wherein the active material is crystalline.
4. The cathode electrode of any one of claims 1-3, wherein the active material is represented by M^1M^2X ,
 wherein M^1 comprises Li, Na, K, or a combination thereof;
 wherein M^2 comprises
 at least one transition metal ion comprising Co, Fe, Mn, Ni, V, Ti, Cr, Cu, Zr, Nb, Ta, Mo, W, Pd, Pt, Re, Cd, or a combination thereof;
 wherein X comprises S, Se, Te, O, or a combination thereof;
 and wherein M^1 , M^2 , and X are present in a predetermined ratio.
5. The cathode electrode of claim 4, wherein the active material further comprises Y and is represented by M^1M^2XY ,
 wherein Y comprises a halogen and wherein M^1 , M^2 , X, and Y are present in a predetermined ratio.
6. The cathode electrode of any one of claims 1-5, wherein the active material further comprises a dopant.
7. The cathode electrode of any one of claims 4-6, wherein the M^2 further comprises a dopant comprising one or more of Mg, Ba, Ca, Sr, Al, B, Ga, Si, Ge, As, Zn, Sn, Sb, In, or any combination thereof.
8. The cathode electrode of any one of claims 1-7, wherein the active material is represented by $M_a^1M_b^2X_cY_d$, wherein M^1 is Na, wherein $2 \leq a \leq 7$, M^2 is one of

- Co, Fe, Mn, Ni, V, Ti, Cr, Cu, Zr, Nb, Ta, Mo, W, Pd, Pt, Re, Cd, or a combination thereof, wherein $0 < b \leq 2$; X is one or more of S, Se, Te, O, or a combination thereof, wherein $2 < c \leq 5$, and Y is a halogen, wherein $0 \leq d \leq 1$.
9. The cathode electrode of claim 8, wherein the M^2 further comprises one or more of Mg, Ba, Ca, Sr, Al, B, Ga, Si, Ge, As, Zn, Sn, Sb, In, or any combination thereof.
 10. The cathode electrode of claim 8 or 9, wherein the M^2 is Co, Fe, Mn, or a combination thereof.
 11. The cathode electrode of any one of claims 8-10, wherein X is S or Se or Te, O, or a combination thereof.
 12. The cathode electrode of any one of claims 8-11, wherein when $d > 0$, Y is Cl, Br, I, F, or a combination thereof.
 13. The cathode electrode of any one of claims 1-12, wherein the active material comprises Na_6CoS_4 .
 14. The cathode electrode of any one of claims 1-13, wherein the active material comprises Na_6FeS_4 .
 15. The cathode electrode of any one of claims 1-14, wherein the active material further comprises a conductive agent.
 16. The cathode electrode of claim 15, wherein the conductive agent comprises one or more of carbon black, carbon nanotubes, graphene, graphite, modified and unmodified carbon, conductive polymers, conductive oxides, conductive ceramics, or any combination thereof.
 17. The cathode electrode of any one of claims 1-16, wherein the active material further comprises a binder.
 18. A secondary battery comprising the cathode electrode of any one of claims 1-17.
 19. The secondary battery of claim 18, wherein the battery further comprises an anode electrode and an electrolyte.

20. The secondary battery of claim 19, wherein the electrolyte is a liquid electrolyte comprising a salt and a solvent.
21. The secondary battery of claim 20, wherein the salt comprises a cation that is a cation of alkali and/or alkaline-earth metal present in the active material.
22. The secondary battery of claim 20 or 21, wherein the salt comprises one or more of sodium fluorophosphate (NaPF_6), sodium fluoroborate (NaBF_4), sodium tetraphenylborate (NaBPh_4), sodium bis(fluorosulfonyl)imide (NaFSI), sodium bis(trifluoromethanesulfonyl)imide (NaTFSI), sodium (fluorosulfonyl)(trifluoromethanesulfonyl)imide (NaFTFSI), sodium perchlorate (NaClO_4), sodium nitrate (NaNO_3), sodium 4,5-dicyano-2-(trifluoromethyl)imidazole (NaTDI), sodium 4,5-dicyano-2-(pentafluoromethyl)imidazole (NaPDI), and sodium difluorooxalato borate (NaDFOB), or any combination thereof.
23. The secondary battery of any one of claims 20-22, wherein the solvent comprises one or more of ethylene carbonate (EC), 1,2-dimethoxyethane (DME), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), 1,2-dimethoxyethane (DME), fluoroethylene carbonate (FEC), tetrahydrofuran (THF), diethylene glycol dimethyl ether (diglyme), triethylene glycol dimethyl ether (TDEM), tetraethylene glycol dimethyl ether (TEGDME), and vinylene carbonate (VC), Bis(2,2,2-trifluoroethyl) ether (BTFE), 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropylether (TTE), tris(2,2,2-trifluoroethyl) orthoformate (TFEO), trimethylphosphate (TMP), triethylphosphate (TEP), or any combination hereof.
24. The secondary battery of any one of claims 20-23, wherein the salt is present in an amount of about 0.01 M to about 3 M.
25. The secondary battery of claim 19, wherein the electrolyte is a solid electrolyte.
26. The secondary battery of any one of claims 20-25, wherein the anode electrode comprises one or more metallic alkali and/or alkaline earth foils, alkali and/or alkaline earth powder, alkali and/or alkaline earth meshes, alkali and/or alkaline earth alloys, carbon materials, non-alkali and/or non-alkaline

earth metal alloys, nonmetal alloys, compound materials, or any combination thereof.

27. The secondary battery of any one of claims 19-26, wherein the anode electrode is a current collector for an alkali metal deposition during a plating step.
28. The secondary battery of any one of claims 18-27, wherein the alkali metal is sodium such that the secondary battery is a sodium-ion battery.
29. The secondary battery of claim 28, wherein the anode electrode comprises an elemental or compound anode suitable for sodium-ion batteries.
30. The secondary battery of any one of claims 18-29, wherein the secondary battery exhibiting a specific capacity of about 100 mAh g⁻¹ to about 600 mAh g⁻¹ at a discharge rate of at least about 0.1C.
31. The secondary battery of claim 30, wherein the secondary battery exhibits a capacity retention of at least about 75% over at least about 200 cycles.
32. The secondary battery of claims 30-31, wherein the secondary battery exhibits a capacity retention of at least about 75% over at least about 500 cycles.
33. The secondary battery of any one of claims 18-32, wherein the secondary battery exhibits coulombic efficiency of greater than about 95%.
34. The secondary battery of any one of claims 18-33, wherein a cathode redox does not involve alkali metal polysulfide formation and/or shuttling.
35. The secondary battery of any one of claims 18-34, wherein the battery is capable of operating in a temperature range of about -30 °C to about 60 °C.
36. A method of making a cathode electrode of any one of claims 1-17, wherein the method comprises:
 - a. forming a mixture comprising an alkali metal or an alkaline-earth metal, one or more transition metals, and a chalcogen-group element;
 - b. heating the mixture to form an active material represented by M¹M²X, wherein M¹ is an alkali metal ion or an alkali-earth metal ion,

wherein M^2 comprises one or more transition metal ions; and
wherein X comprises at least one chalcogen anion, and wherein M^1 , M^2 , and X are present in a predetermined ratio.

37. The method of claim 36, wherein M^1 is Li, Na, K, or a combination thereof.
38. The method of claim 36 or 37, wherein M^2 is Co, Fe, Mn, Ni, Al, B, V, Ti, Cr, Cu, Ga, Si, Ge, As, Zr, Nb, Ta, Mo, W, Pd, Pt, Re, Cd, or a combination thereof.
39. The method of any one of claims 36-38, wherein X is an anion of S, Se, Te, O, or a combination thereof.
40. The method of any one of claims 36-39, wherein the M^2 further comprises one or more of Mg, Ba, Ca, Sr, Al, B, Ga, Si, Ge, As, Zn, Sn, Sb, In, or any combination thereof.
41. The method of any one of claims 36-40, wherein the active material further comprises Y and is represented by M^1M^2XY , wherein Y comprises a halogen, and wherein M^1 , M^2 , X, and Y are present in a predetermined ratio.
42. The method of claim 41, wherein the active material is represented by $M_a^1M_b^2X_cY_d$, wherein M^1 is Na, wherein $2 \leq a \leq 7$, M^2 is one of Co, Fe, Mn, Ni, V, Ti, Cr, Cu, Zr, Nb, Ta, Mo, W, Pd, Pt, Re, Cd, or a combination thereof, wherein $0 < b \leq 2$; X is one or more of S, Se, Te, O, or a combination thereof, wherein $2 < c \leq 5$, and Y is a halogen, wherein $0 \leq d \leq 1$.
43. The method of any one of claims 36-42, wherein at least one of the alkali metal, alkaline-earth metal, the one or more transition metals, and the chalcogen-group element in the mixture are present as an ion.
44. The method of any one of claims 36-42, wherein at least one of the alkali metal, alkaline-earth metal, the one or more transition metals, and the chalcogen-group element in the mixture are present in zero valence.
45. The method of any one of claims 36-43, wherein the mixture is formed in a first solvent.
46. The method of claim 45, wherein the first solvent is an aqueous solution, an organic solvent, or a combination thereof.

47. The method of any one of claims 36-46, wherein the mixture further comprises a reducing or an oxidating agent.
48. The method of any one of claims 36-47, wherein the mixture comprises a reducing agent comprising carbon.
49. The method of any one of claims 36-48, wherein the mixture further comprises a conductive agent, a binder, or a combination thereof.
50. The method of any one of claims 36-49, wherein the heating of the mixture is performed at a temperature of 500 °C - 1000 °C in one or more heating steps.
51. The method of any one of claims 36-50, further comprising forming a slurry of the active material and a binder in a second solvent.
52. The method of claim 51, wherein the second solvent comprises one or more organic solvents.
53. The method of claim 51 or 52, wherein the slurry is disposed on a substrate and the second solvent is substantially removed.
54. A method comprising:
 - providing the cathode electrode of any one of claims 1-17;
 - providing an anode electrode;
 - providing an electrolyte; and
 - providing a separator;
 - forming the secondary battery of any one of claims 18-35.

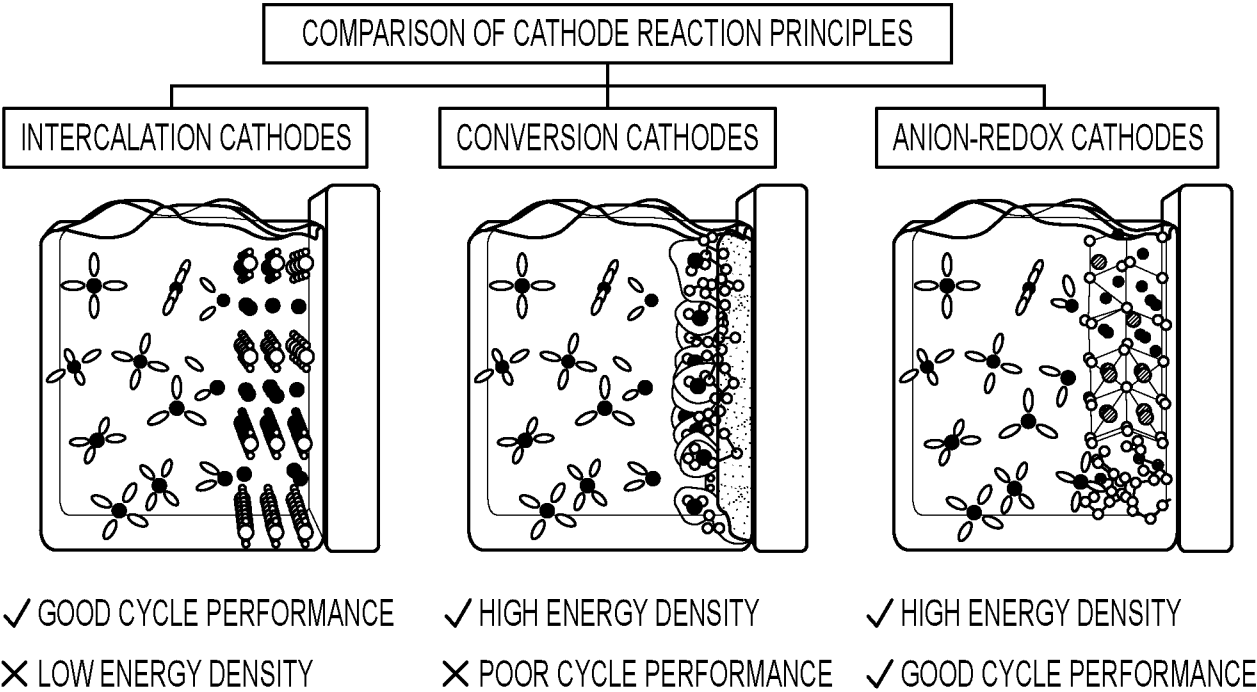


FIG. 1A

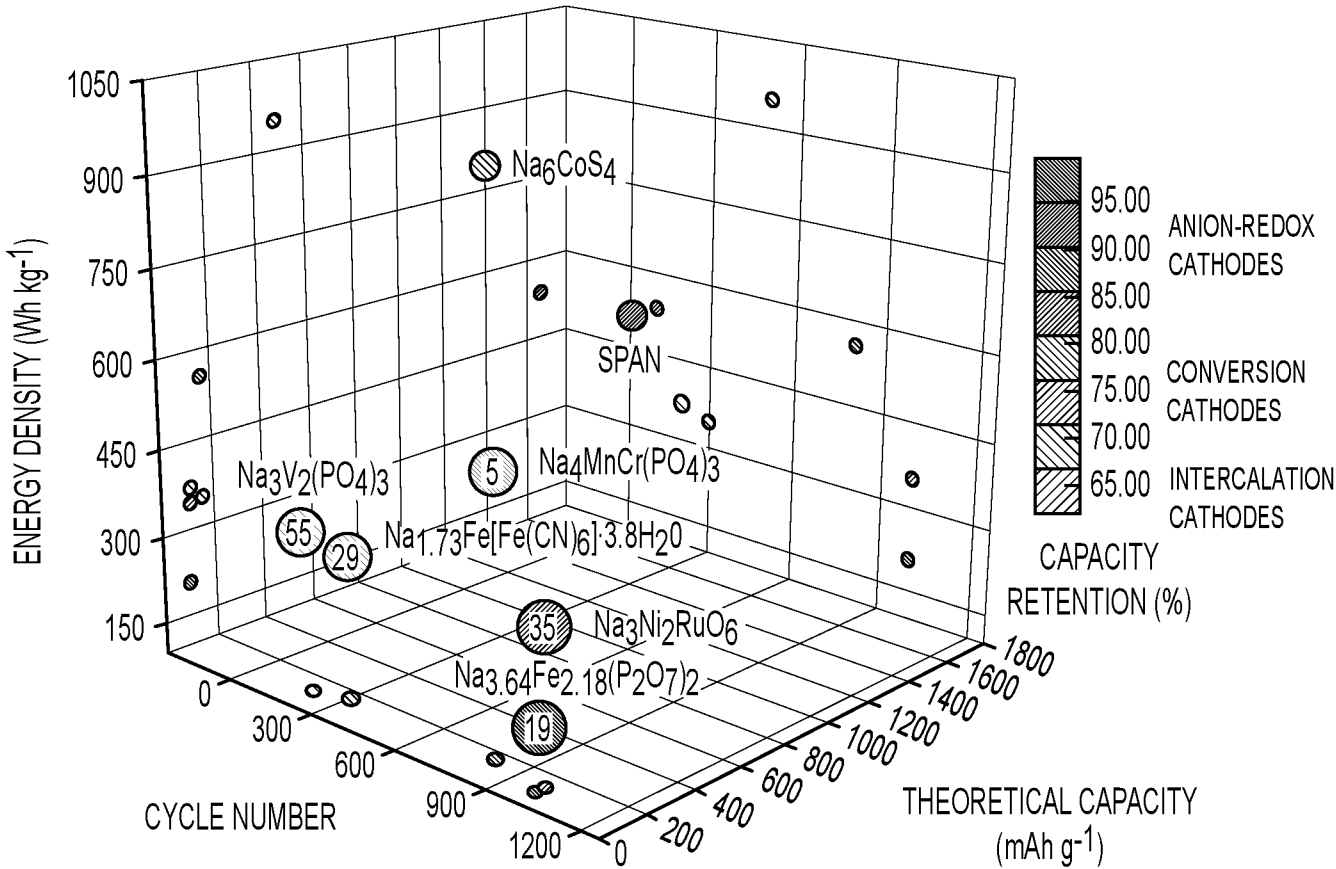
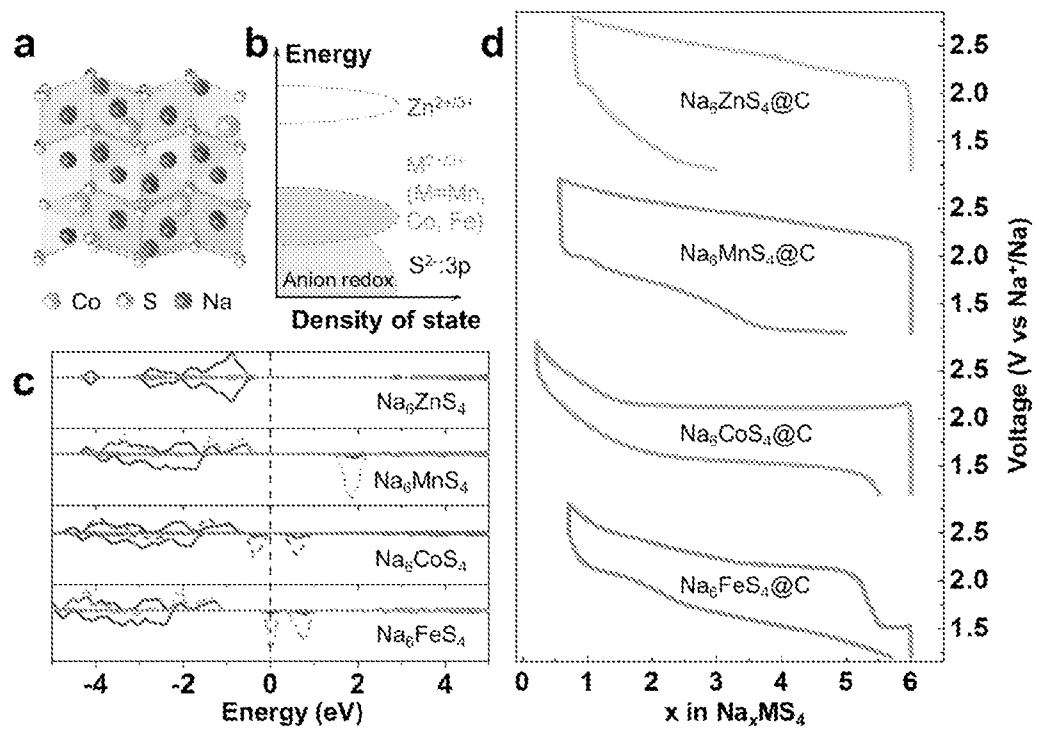


FIG. 1B



FIGs. 2A-2D

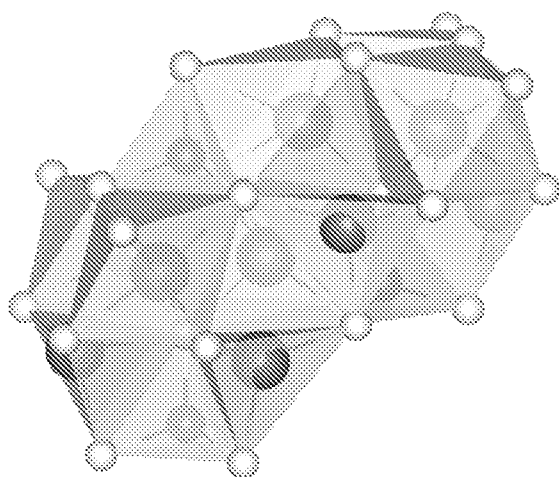
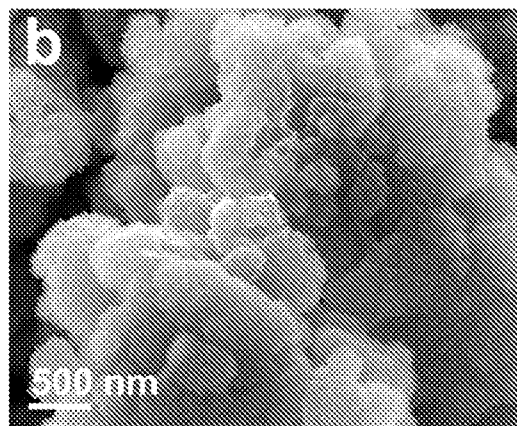
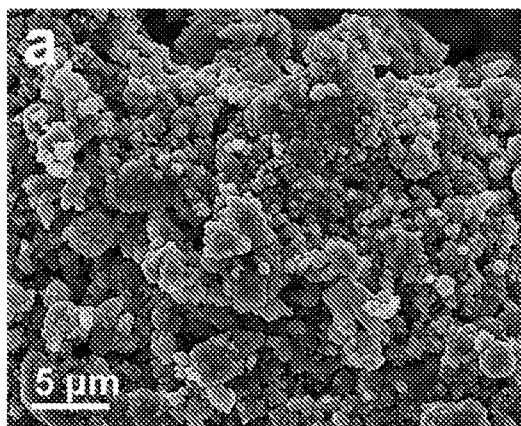


FIG. 2E



FIGs. 3A-3B

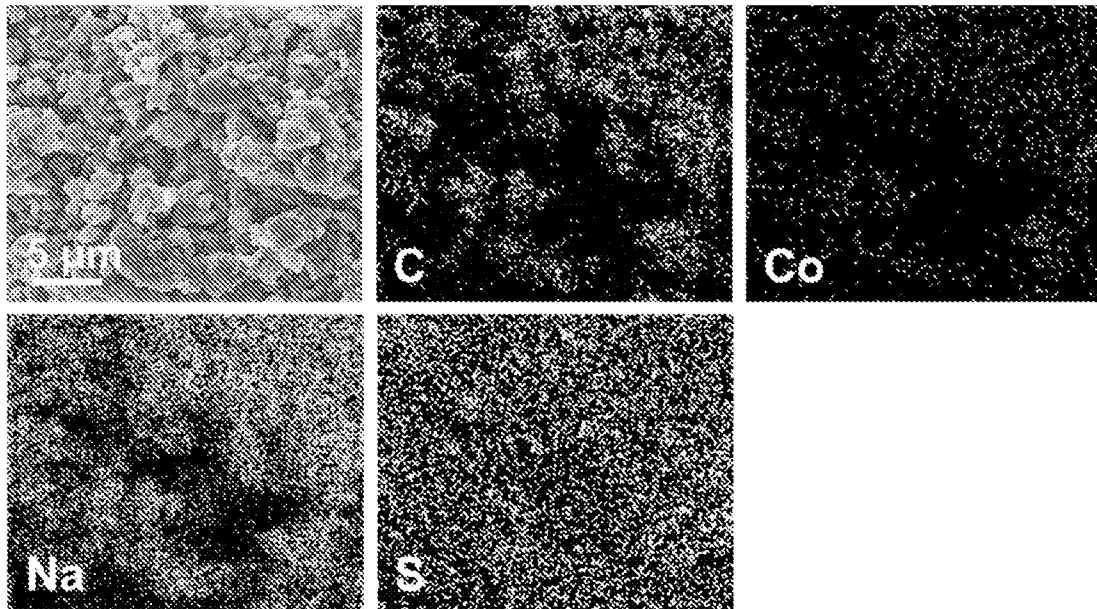


FIG. 3C

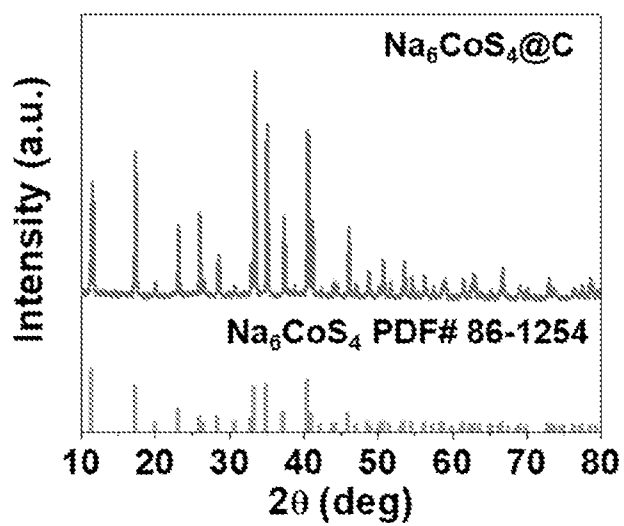


FIG. 4

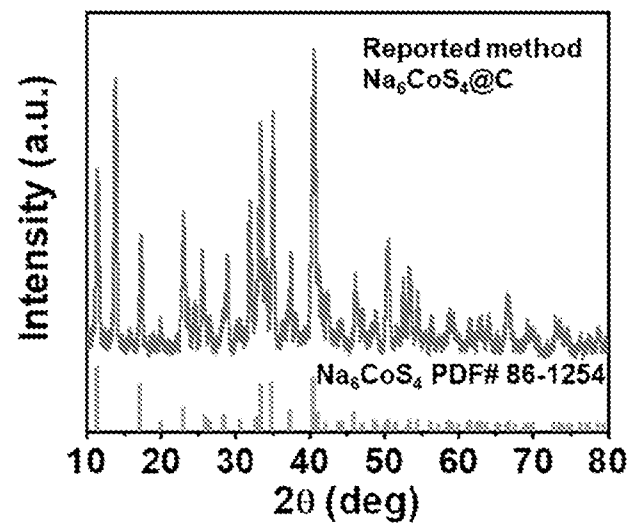
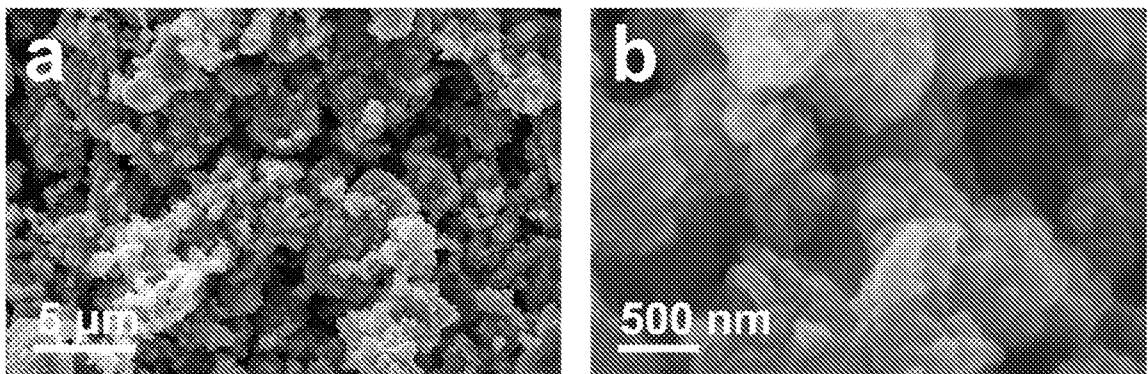


FIG. 5



FIGs. 6A-6B

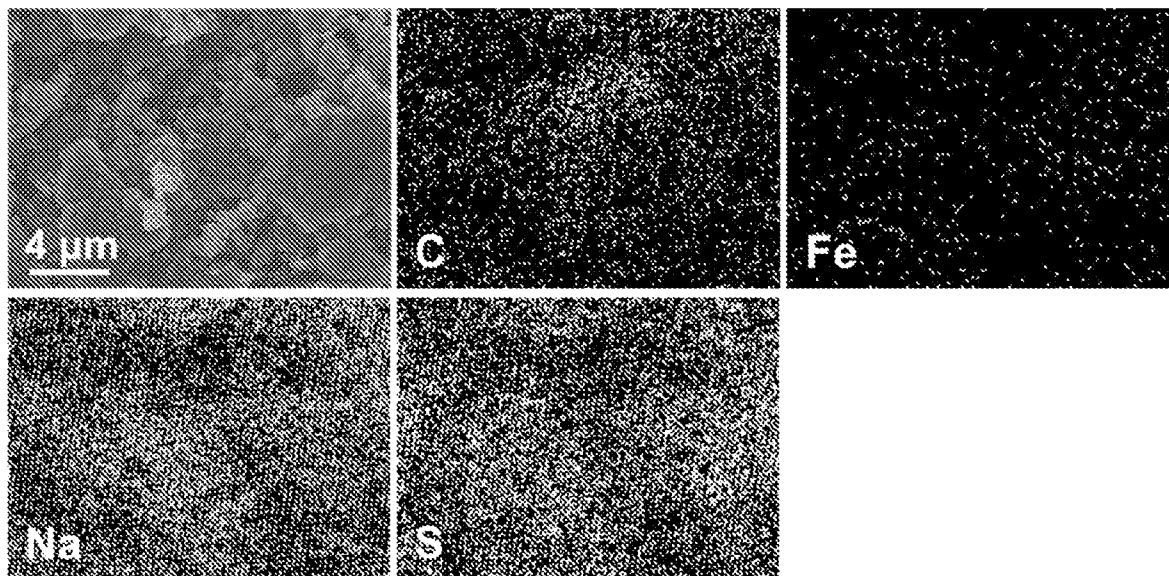


FIG. 7

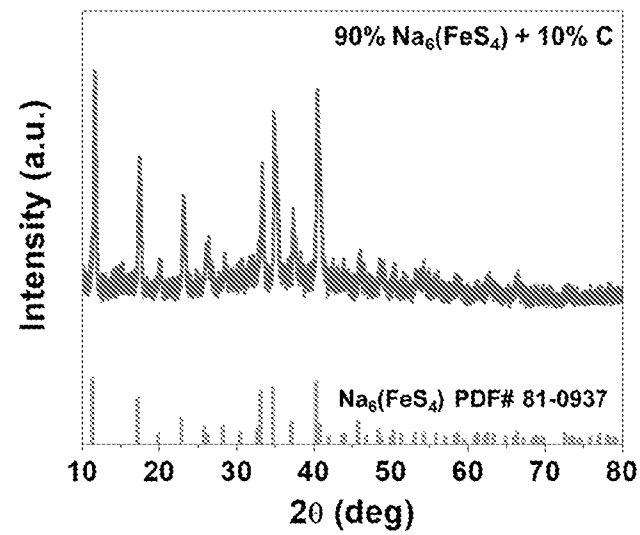


FIG. 8

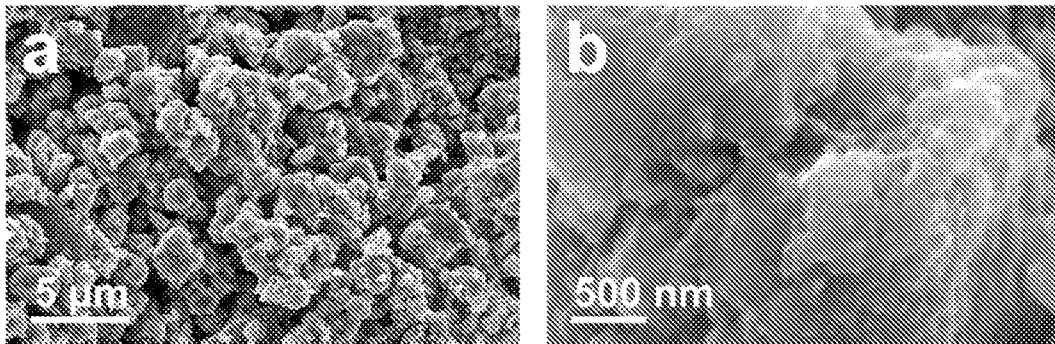


FIG. 9A-9B

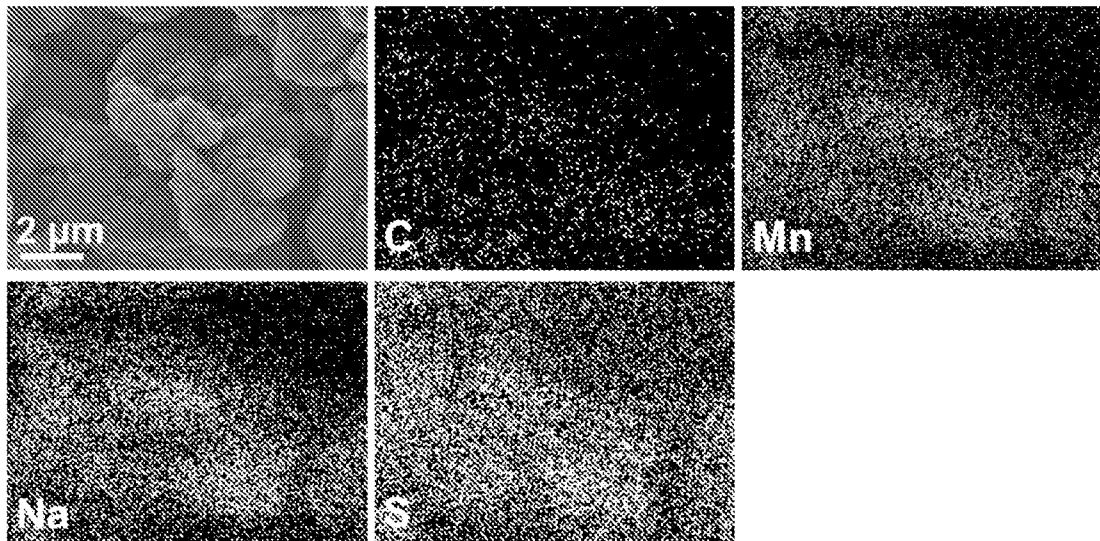


FIG. 10

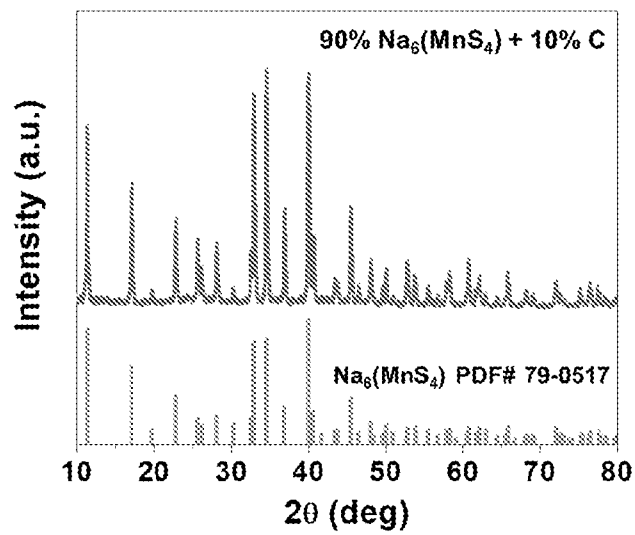
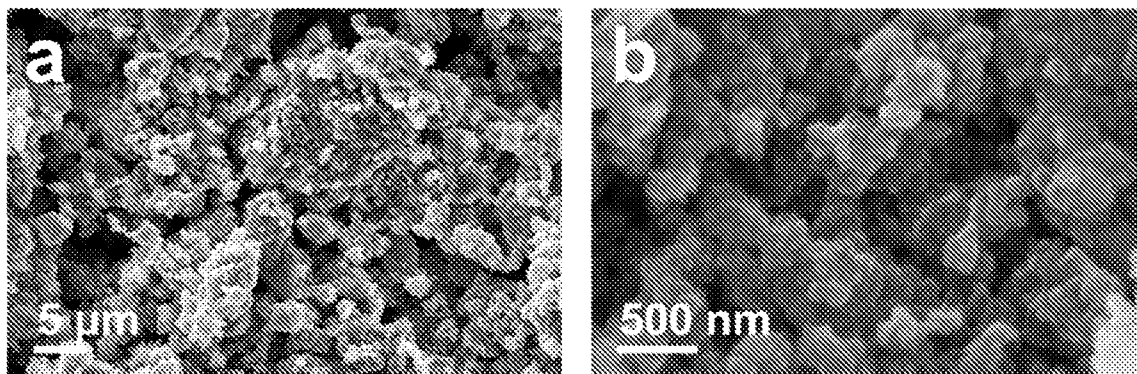


FIG. 11



FIGs. 12A-12B

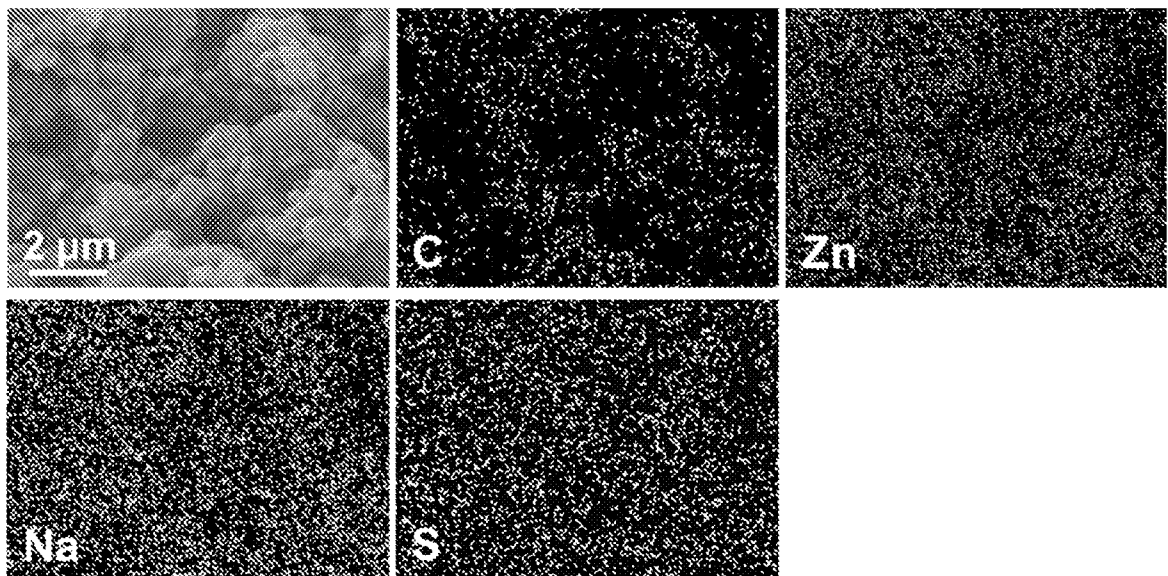


FIG. 13

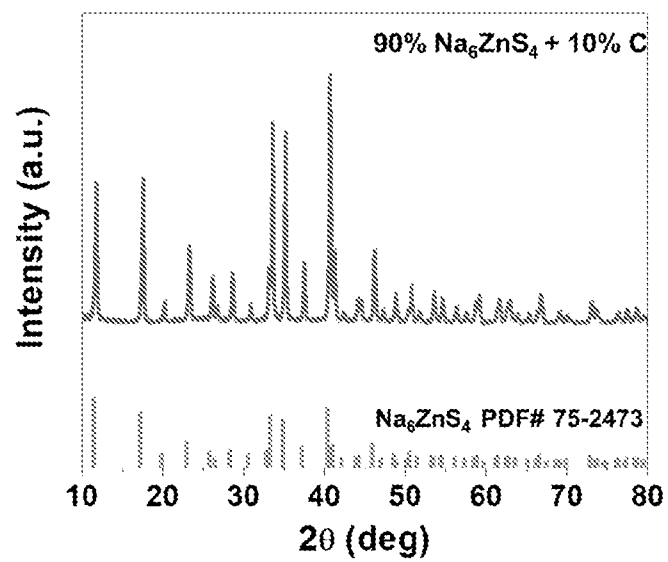


FIG. 14

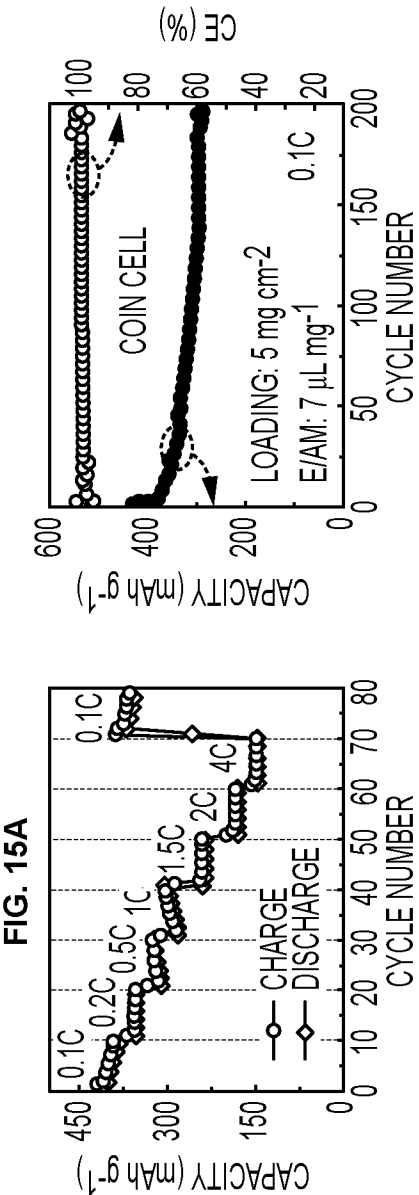
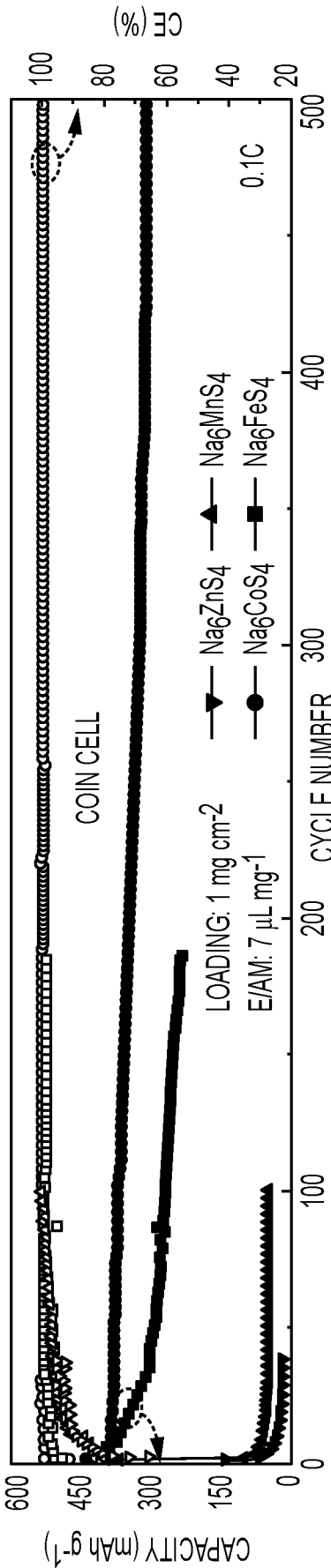


FIG. 15A

FIG. 15B

FIG. 15C

FIG. 15D

FIG. 15E

FIG. 15F

FIG. 15G

FIG. 15H

FIG. 15I

FIG. 15J

FIG. 15K

FIG. 15L

FIG. 15M

FIG. 15N

FIG. 15O

FIG. 15P

FIG. 15Q

FIG. 15R

FIG. 15S

FIG. 15T

FIG. 15U

FIG. 15V

FIG. 15W

FIG. 15X

FIG. 15Y

FIG. 15Z

FIG. 15AA

FIG. 15AB

FIG. 15AC

FIG. 15AD

FIG. 15AE

FIG. 15AF

FIG. 15AG

FIG. 15AH

FIG. 15AI

FIG. 15AJ

FIG. 15AK

FIG. 15AL

FIG. 15AM

FIG. 15AN

FIG. 15AO

FIG. 15AP

FIG. 15AQ

FIG. 15AR

FIG. 15AS

FIG. 15AT

FIG. 15AU

FIG. 15AV

FIG. 15AW

FIG. 15AX

FIG. 15AY

FIG. 15AZ

FIG. 15BA

FIG. 15BB

FIG. 15BC

FIG. 15BD

FIG. 15BE

FIG. 15BF

FIG. 15BG

FIG. 15BH

FIG. 15BI

FIG. 15BJ

FIG. 15BK

FIG. 15BL

FIG. 15BM

FIG. 15BN

FIG. 15BO

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FIG. 15BQ

FIG. 15BR

FIG. 15BS

FIG. 15BT

FIG. 15BU

FIG. 15BV

FIG. 15BW

FIG. 15BX

FIG. 15BY

FIG. 15BZ

FIG. 15CA

FIG. 15CB

FIG. 15CC

FIG. 15CD

FIG. 15CE

FIG. 15CF

FIG. 15CG

FIG. 15CH

FIG. 15CI

FIG. 15CJ

FIG. 15CK

FIG. 15CL

FIG. 15CM

FIG. 15CN

FIG. 15CO

FIG. 15CP

FIG. 15CQ

FIG. 15CR

FIG. 15CS

FIG. 15CT

FIG. 15CU

FIG. 15CV

FIG. 15CW

FIG. 15CX

FIG. 15CY

FIG. 15CZ

FIG. 15DA

FIG. 15DB

FIG. 15DC

FIG. 15DD

FIG. 15DE

FIG. 15DF

FIG. 15DG

FIG. 15DH

FIG. 15DI

FIG. 15DJ

FIG. 15DK

FIG. 15DL

FIG. 15DM

FIG. 15DN

FIG. 15DO

FIG. 15DP

FIG. 15DQ

FIG. 15DR

FIG. 15DS

FIG. 15DT

FIG. 15DU

FIG. 15DV

FIG. 15DW

FIG. 15DX

FIG. 15DY

FIG. 15DZ

FIG. 15EA

FIG. 15EB

FIG. 15EC

FIG. 15ED

FIG. 15EE

FIG. 15EF

FIG. 15EG

FIG. 15EH

FIG. 15EI

FIG. 15EJ

FIG. 15EK

FIG. 15EL

FIG. 15EM

FIG. 15EN

FIG. 15EO

FIG. 15EP

FIG. 15EQ

FIG. 15ER

FIG. 15ES

FIG. 15ET

FIG. 15EU

FIG. 15EV

FIG. 15EW

FIG. 15EX

FIG. 15EY

FIG. 15EZ

FIG. 15FA

FIG. 15FB

FIG. 15FC

FIG. 15FD

FIG. 15FE

FIG. 15FF

FIG. 15FG

FIG. 15FH

FIG. 15FI

FIG. 15FJ

FIG. 15FK

FIG. 15FL

FIG. 15FM

FIG. 15FN

FIG. 15FO

FIG. 15FP

FIG. 15FQ

FIG. 15FR

FIG. 15FS

FIG. 15FT

FIG. 15FU

FIG. 15FV

FIG. 15FW

FIG. 15FX

FIG. 15FY

FIG. 15FZ

FIG. 15GA

FIG. 15GB

FIG. 15GC

FIG. 15GD

FIG. 15GE

FIG. 15GF

FIG. 15GG

FIG. 15GH

FIG. 15GI

FIG. 15GJ

FIG. 15GK

FIG. 15GL

FIG. 15GM

FIG. 15GN

FIG. 15GO

FIG. 15GP

FIG. 15GQ

FIG. 15GR

FIG. 15GS

FIG. 15GT

FIG. 15GU

FIG. 15GV

FIG. 15GW

FIG. 15GX

FIG. 15GY

FIG. 15GZ

FIG. 15HA

FIG. 15HB

FIG. 15HC

FIG. 15HD

FIG. 15HE

FIG. 15HF

FIG. 15HG

FIG. 15HH

FIG. 15HI

FIG. 15HJ

FIG. 15HK

FIG. 15HL

FIG. 15HM

FIG. 15HN

FIG. 15HO

FIG. 15HP

FIG. 15HQ

FIG. 15HR

FIG. 15HS

FIG. 15HT

FIG. 15HU

FIG. 15HV

FIG. 15HW

FIG. 15HX

FIG. 15HY

FIG. 15HZ

FIG. 15IA

FIG. 15IB

FIG. 15IC

FIG. 15ID

FIG. 15IE

FIG. 15IF

FIG. 15IG

FIG. 15IH

FIG. 15II

FIG. 15IJ

FIG. 15IK

FIG. 15IL

FIG. 15IM

FIG. 15IN

FIG. 15IO

FIG. 15IP

FIG. 15IQ

FIG. 15IR

FIG. 15IS

FIG. 15IT

FIG. 15IU

FIG. 15IV

FIG. 15IW

FIG. 15IX

FIG. 15IY

FIG. 15IZ

FIG. 15JA

FIG. 15JB

FIG. 15JC

FIG. 15JD

FIG. 15JE

FIG. 15JF

FIG. 15JG

FIG. 15JH

FIG. 15JI

FIG. 15JJ

FIG. 15JK

FIG. 15JL

FIG. 15JM

FIG. 15JN

FIG. 15JO

FIG. 15JP

FIG. 15JQ

FIG. 15JR

FIG. 15JS

FIG. 15JT

FIG. 15JU

FIG. 15JV

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FIG. 15JX

FIG. 15JY

FIG. 15JZ

FIG. 15KA

FIG. 15KB

FIG. 15KC

FIG. 15KD

FIG. 15KE

FIG. 15KF

FIG. 15KG

FIG. 15KH

FIG. 15KI

FIG. 15KJ

FIG. 15KK

FIG. 15KL

FIG. 15KM

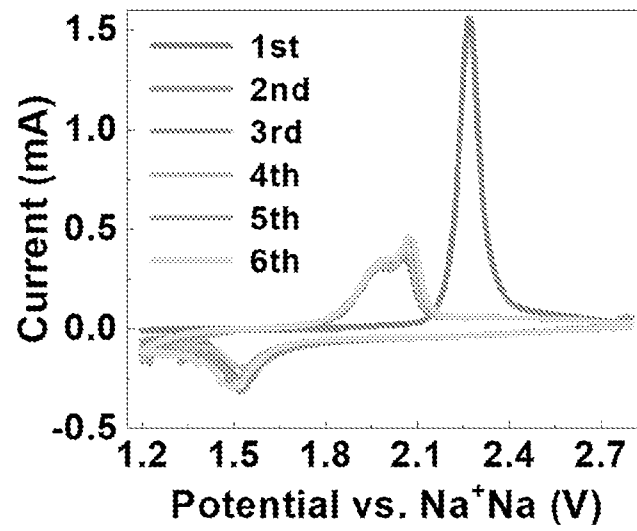
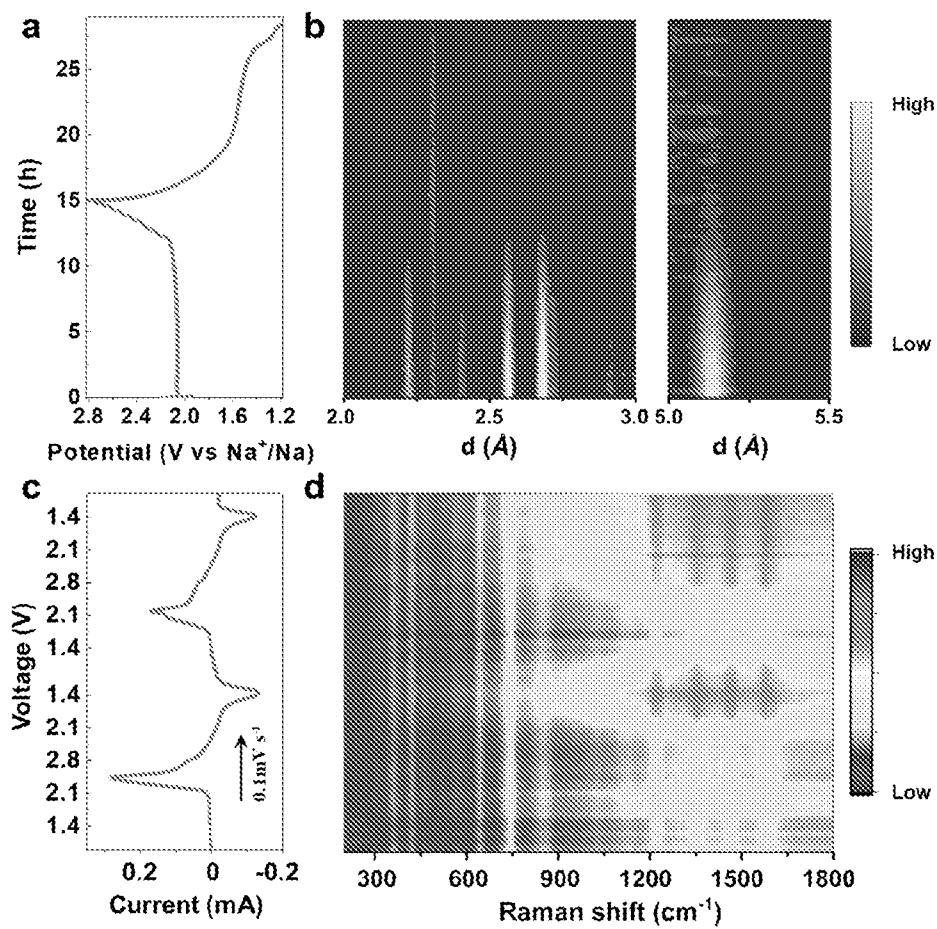
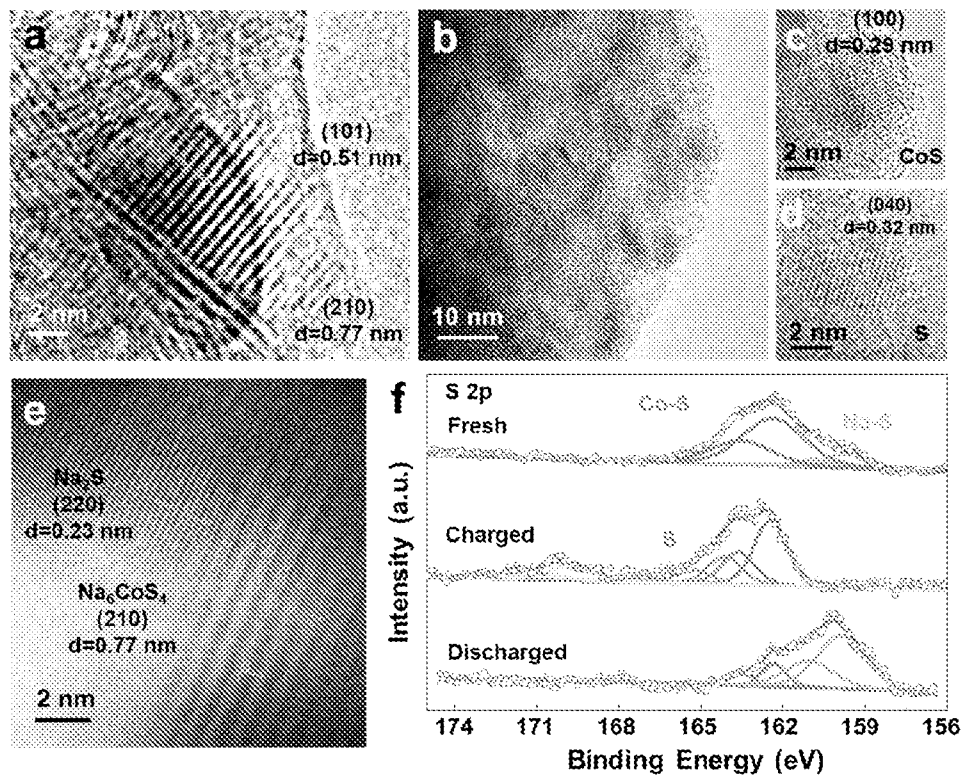


FIG. 16



FIGs. 17A-17D



FIGs. 18A-18F

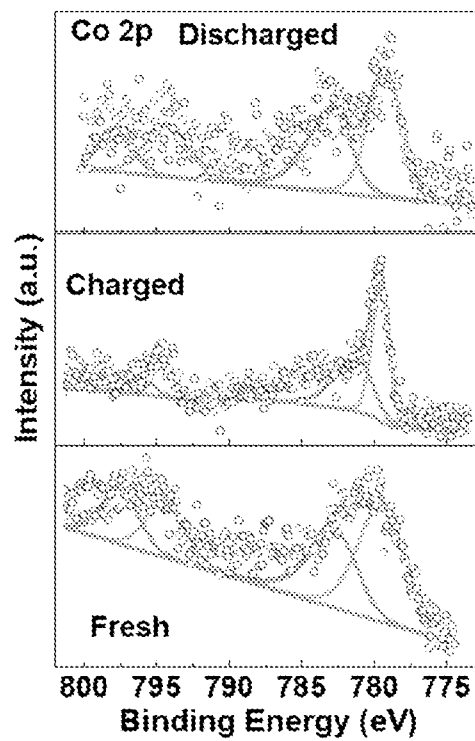
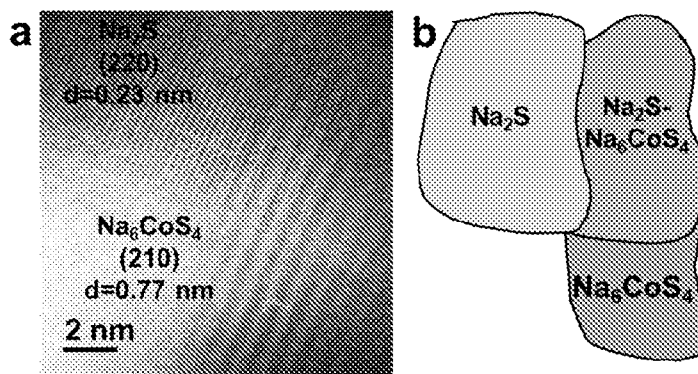


FIG. 19



FIGs. 20A-20B

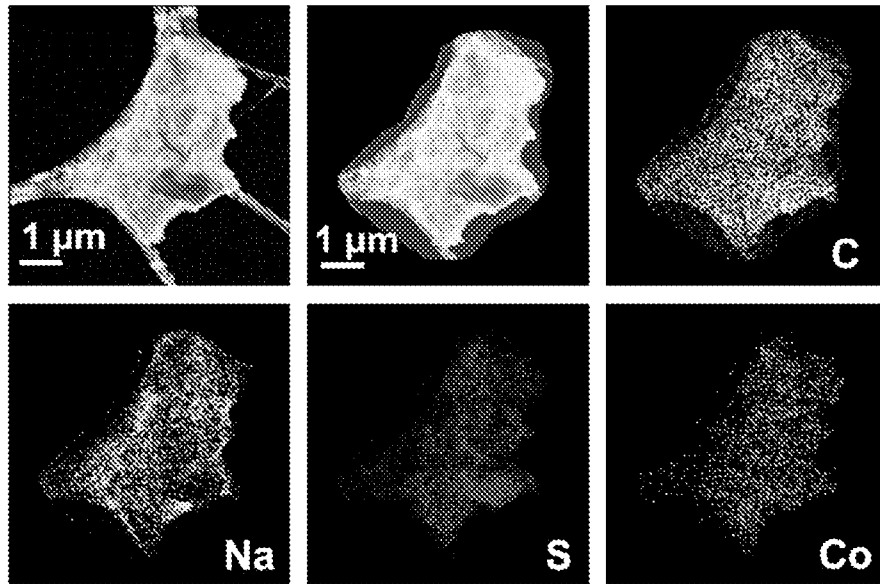


FIG. 21

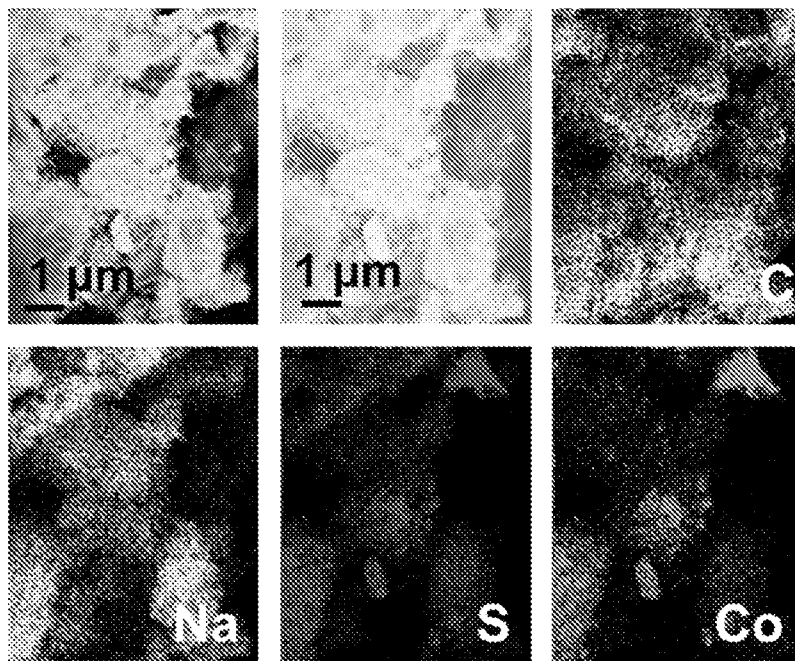


FIG. 22

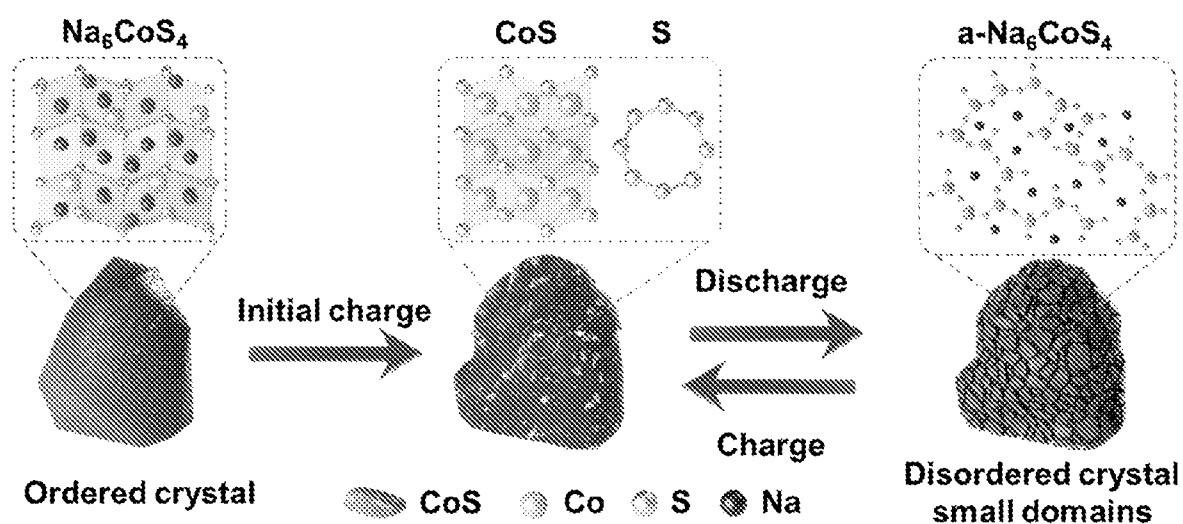


FIG. 23

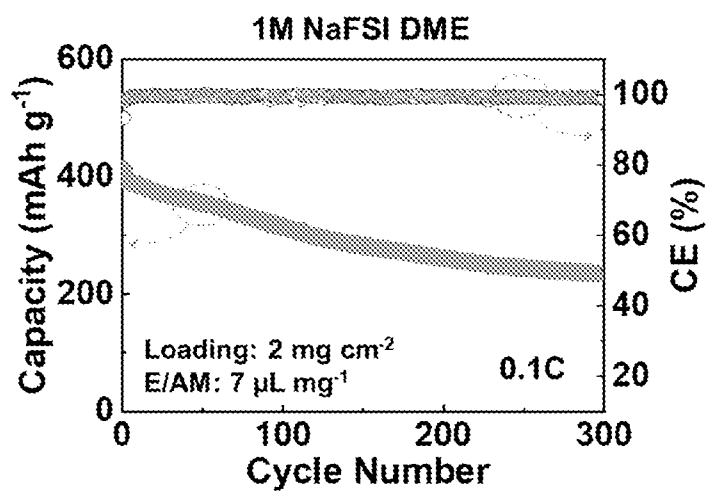


FIG. 24

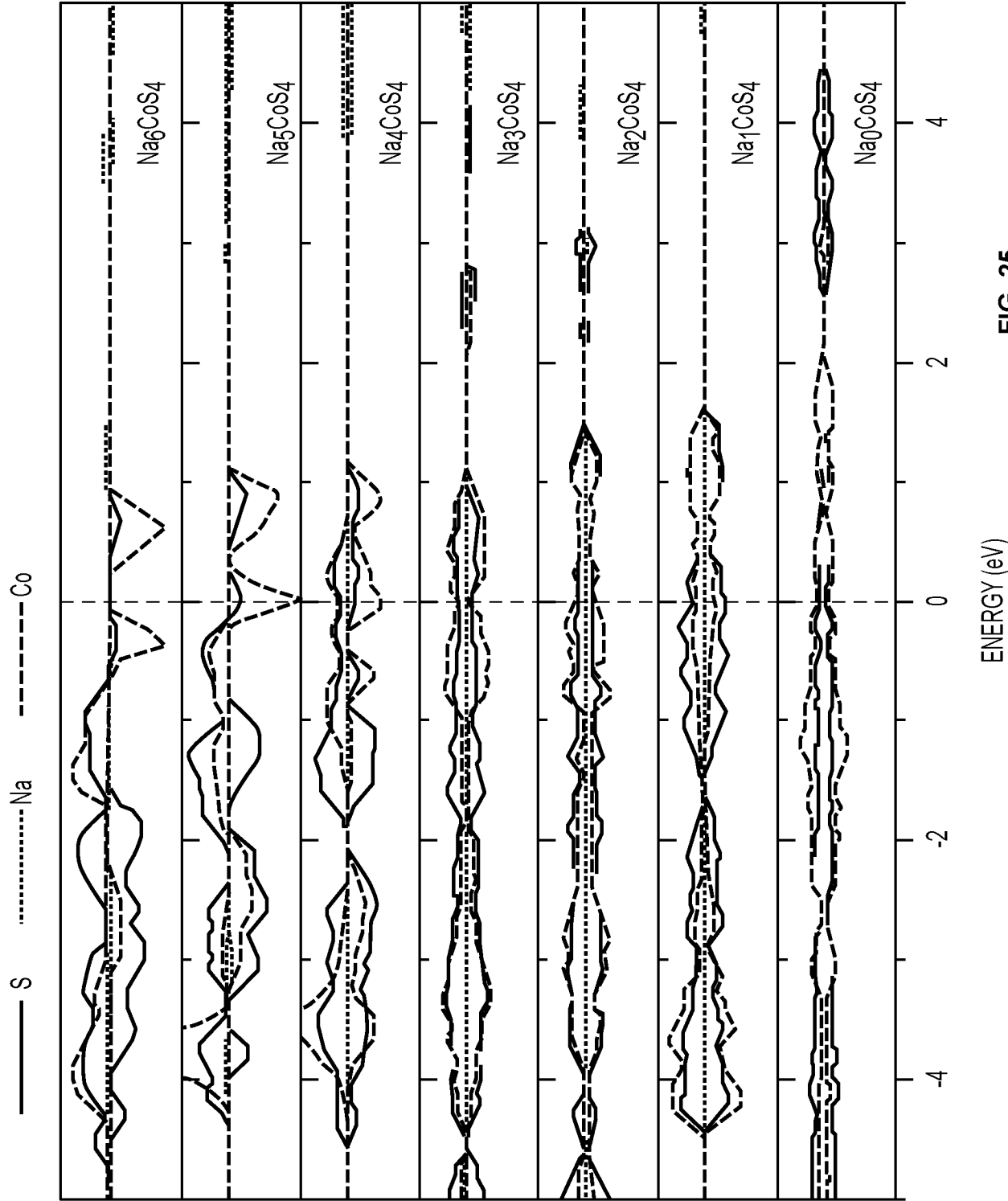


FIG. 25

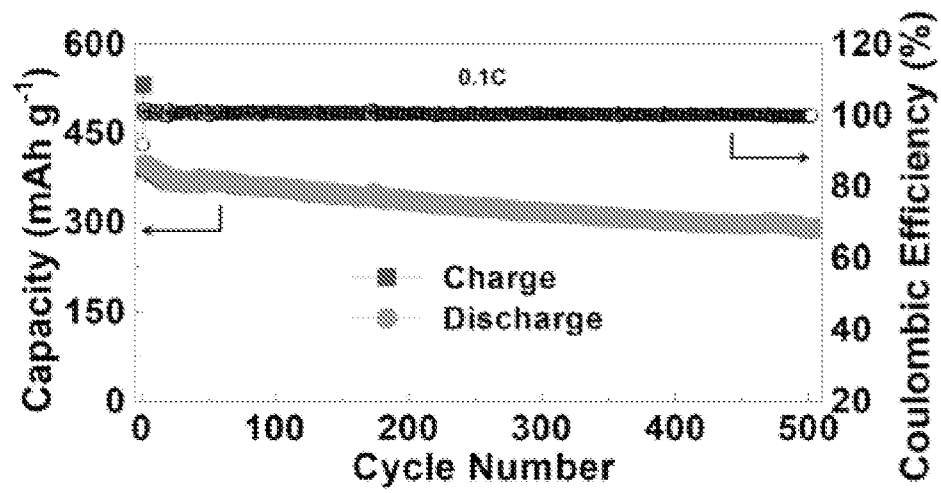


FIG. 26

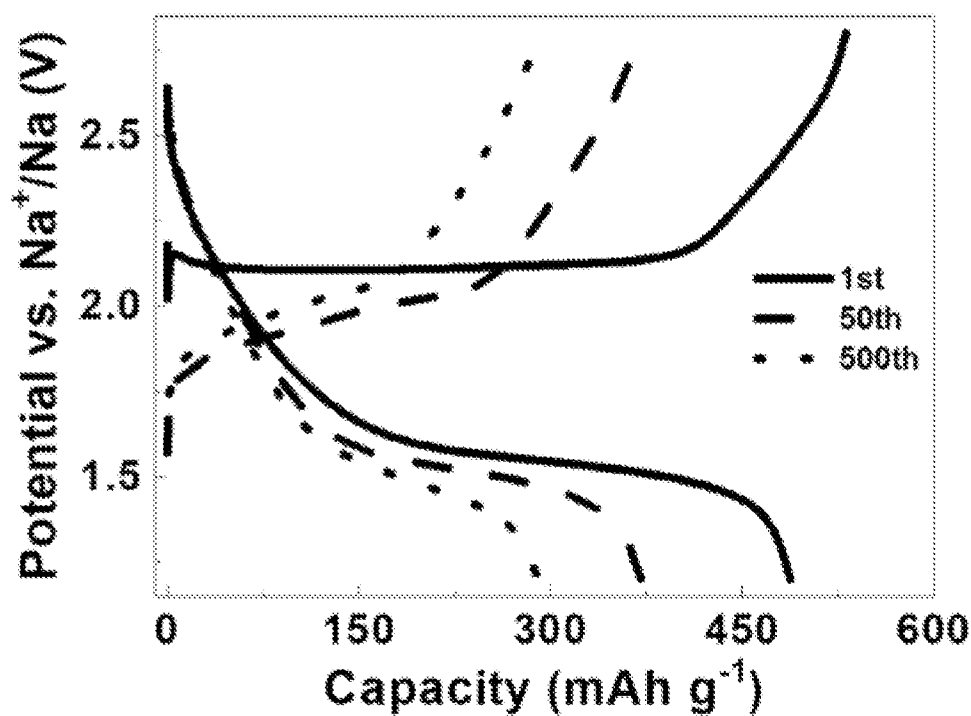


FIG. 27

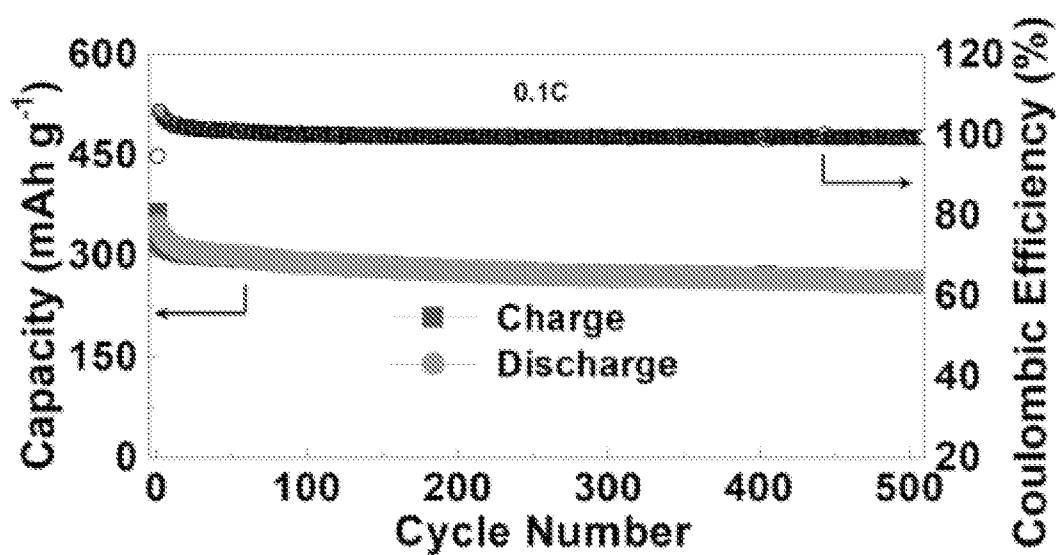


FIG. 28

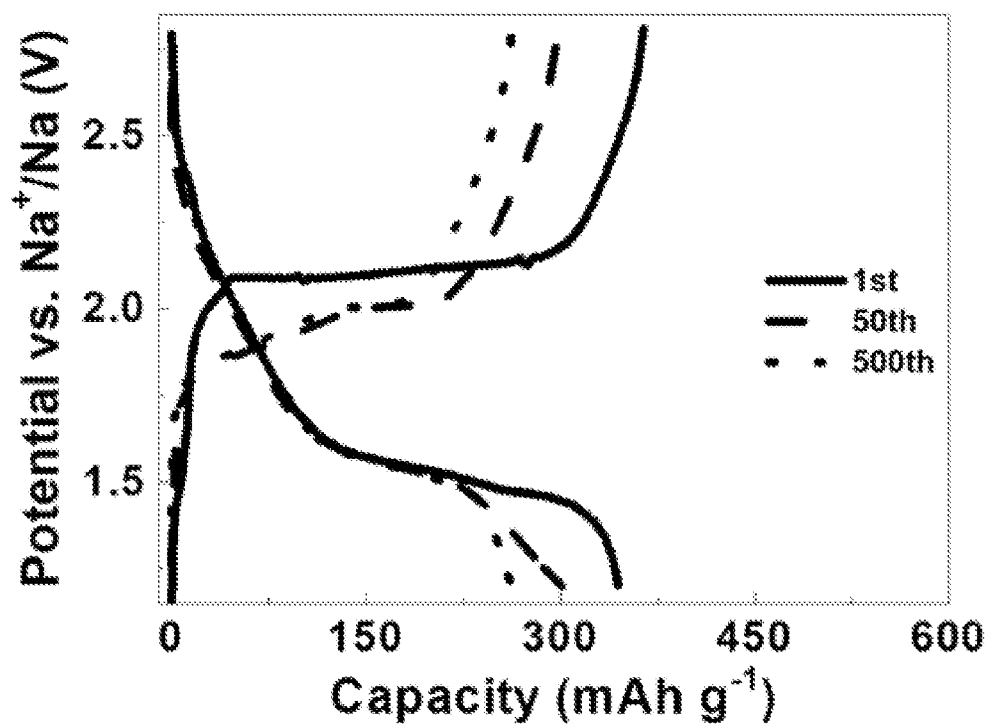


FIG. 29

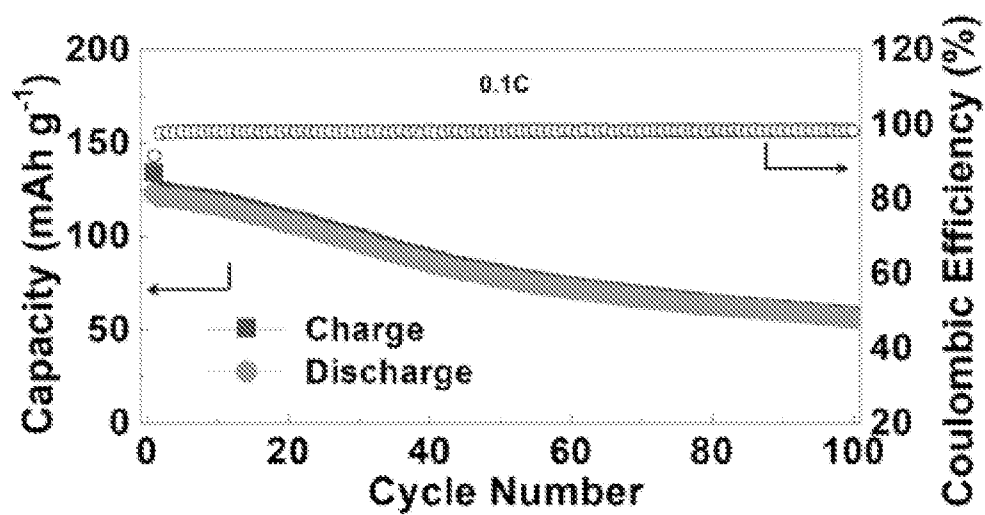


FIG. 30

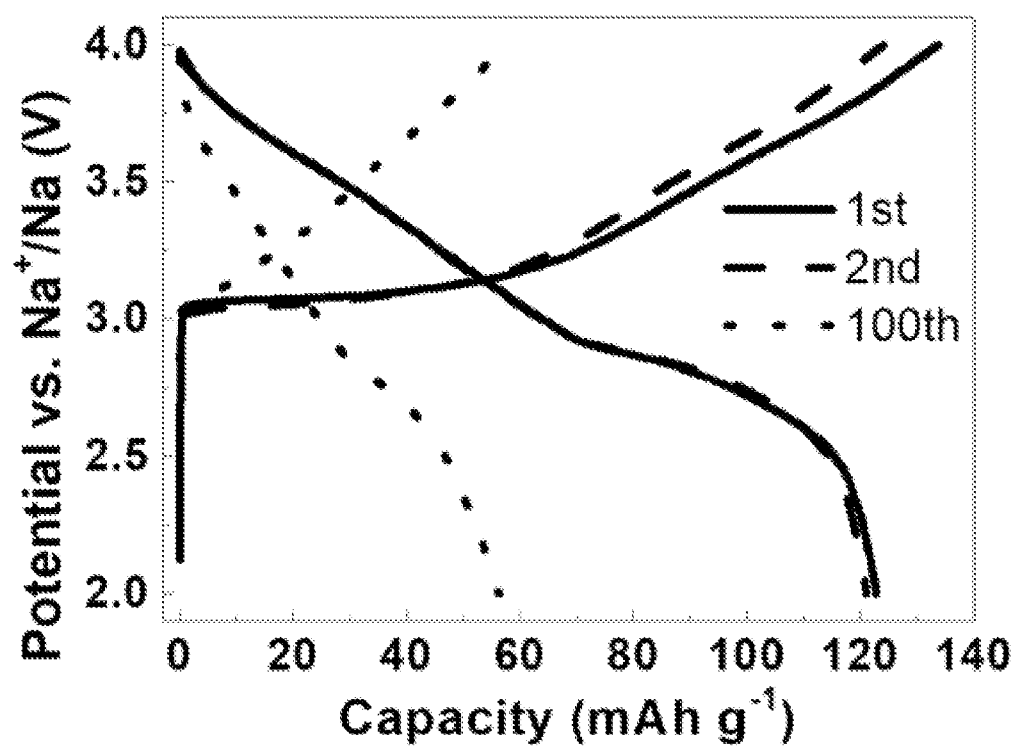


FIG. 31

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2024/029049

A. CLASSIFICATION OF SUBJECT MATTERIPC: **H01M 4/62** (2024.01); **H01M 10/0525** (2024.01); **H01G 11/30** (2024.01)CPC: **H01M 4/62**; **H01M 10/0525**; **H01G 11/30**

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)

See Search History Document

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

See Search History Document

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

See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2023/019322 A1 (DEAKIN UNIVERSITY) 23 February 2023 (23.02.2023)	1, 2
Y	entire document	3
Y	US 2018/0159123 A1 (TOYOTA MOTOR ENGINEERING & MANUFACTURING NORTH AMERICA INC.) 07 June 2018 (07.06.2018) entire document	3
A	US 2021/0320296 A1 (ALBEMARLE GERMANY GMBH) 14 October 2021 (14.10.2021) entire document	1-3
A	US 2021/0194042 A1 (NORTHWESTERN UNIVERSITY et al.) 24 June 2021 (24.06.2021) entire document	1-3
A	US 2017/0098824 A1 (QUANTUMSCAPE CORPORATION) 06 April 2017 (06.04.2017) entire document	1-3
A	US 2020/0343580 A1 (SILA NANOTECHNOLOGIES INC.) 29 October 2020 (29.10.2020) entire document	1-3



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

“D” document cited by the applicant in the international application

“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

04 July 2024 (04.07.2024)

Date of mailing of the international search report

29 July 2024 (29.07.2024)

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US
Commissioner for Patents
P.O. Box 1450, Alexandria, VA 22313-1450

Facsimile No. 571-273-8300

Authorized officer

MATOS
TAINA

Telephone No. 571-272-4300

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2024/029049

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.:
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:
3. ☒ Claims Nos.: **4-54**
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).