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(54) **ALLOY COMPOSITIONS FOR LITHIUM ION BATTERIES**

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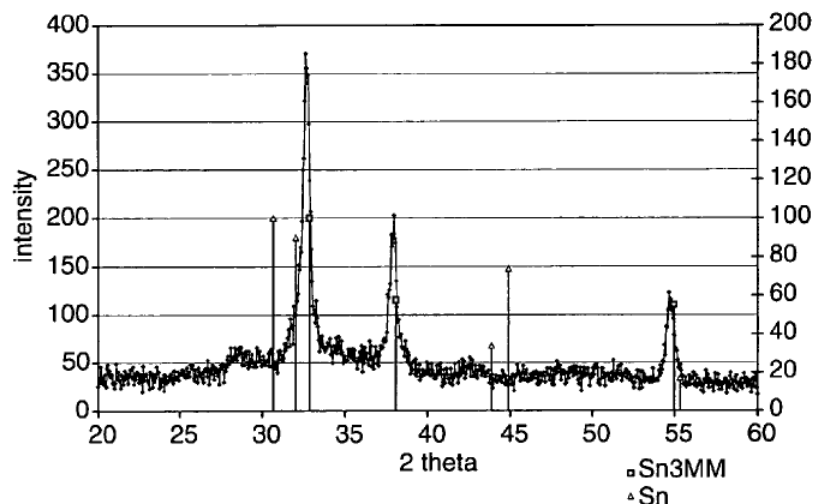
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(57) **ABSTRACT**

Alloy compositions, lithium ion batteries, and methods of making lithium ion batteries are described. The lithium ion batteries have anodes that contain an alloy composition that includes a) silicon, b) aluminum, c) transition metal, d) tin, and e) a fifth element that contains yttrium, a lanthanide element, an actinide element, or a combination thereof. The alloy composition is a mixture of an amorphous phase that includes silicon and a nanocrystalline phase that includes an intermetallic compound of tin and the fifth element.

23 Claims, 3 Drawing Sheets



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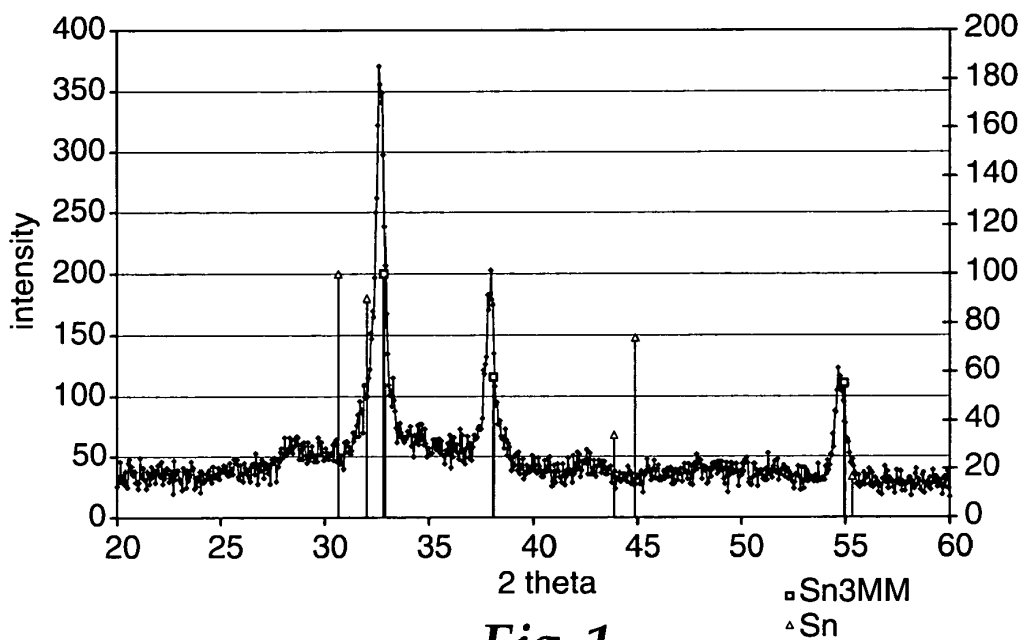
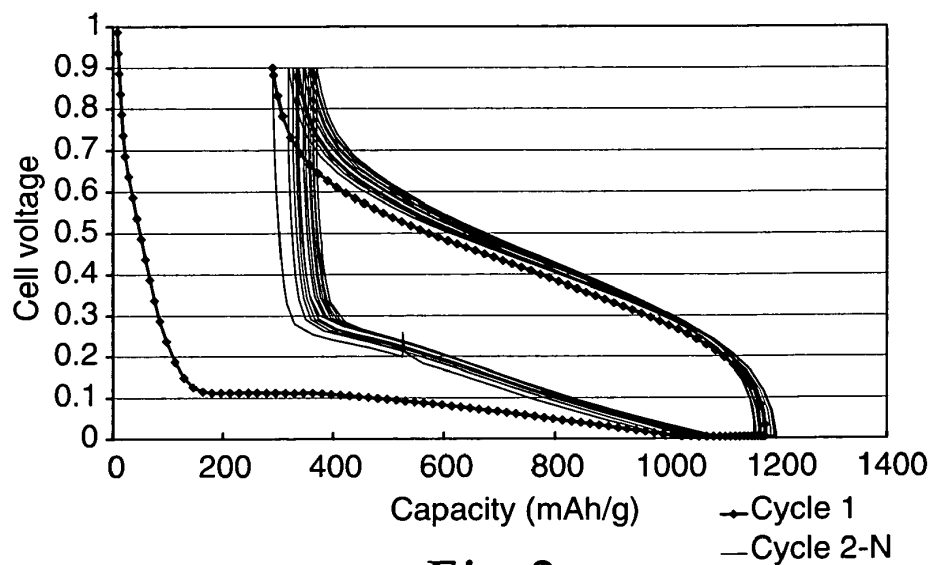
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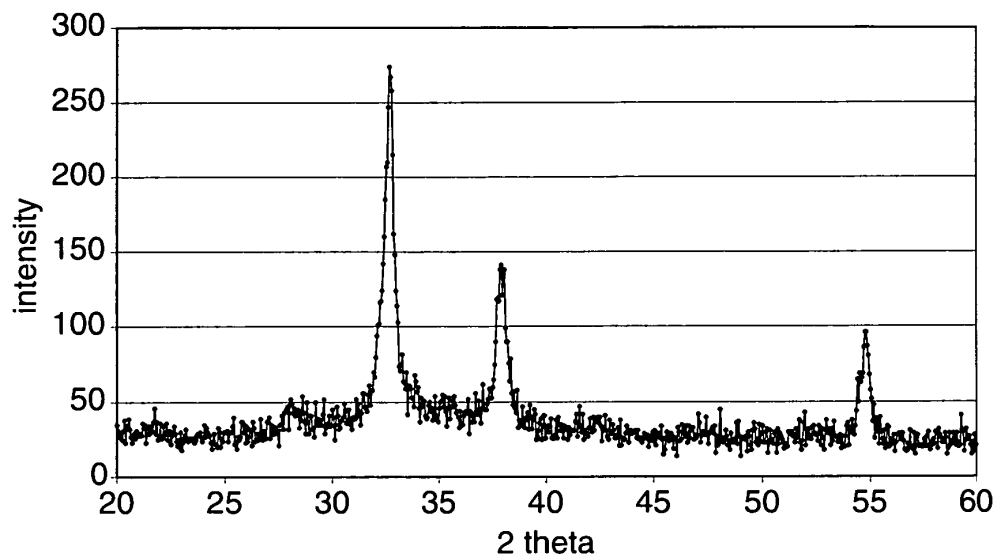
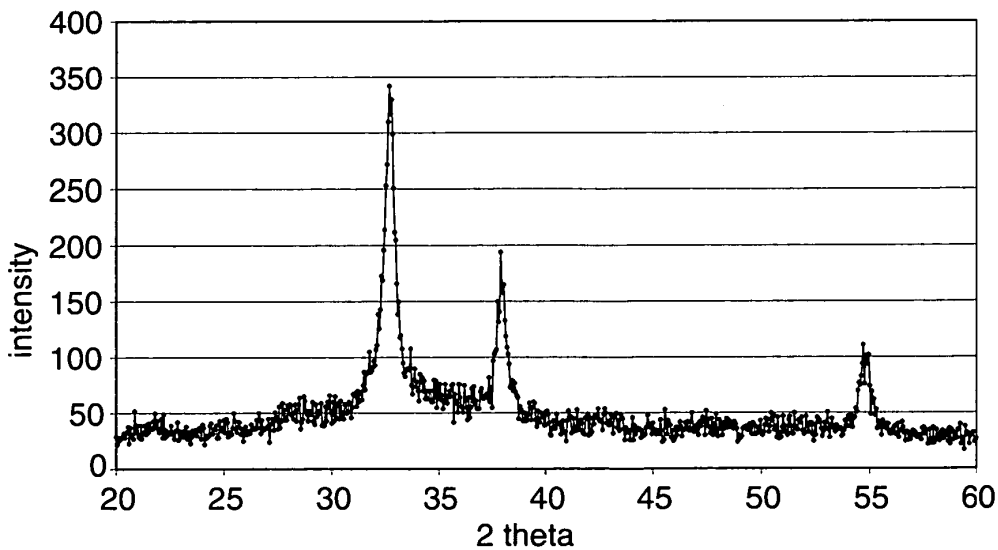
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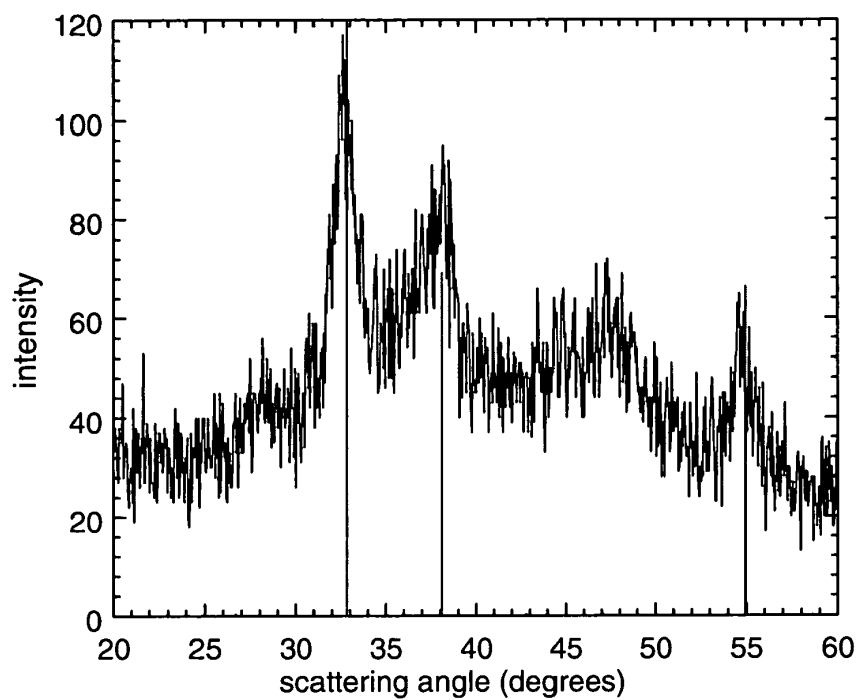
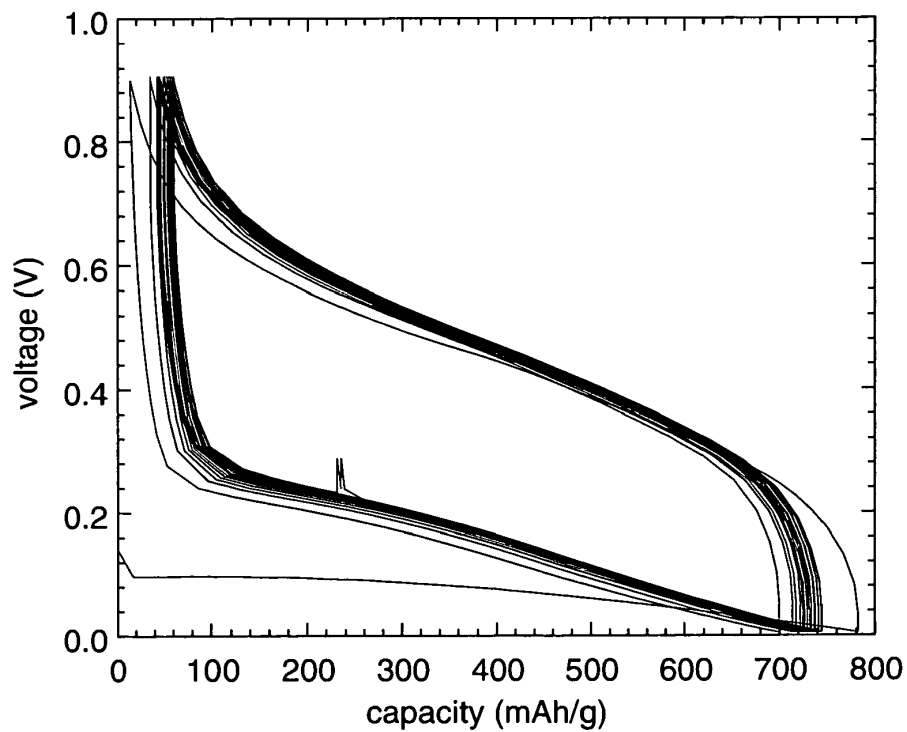
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*Fig. 1**Fig. 2*

*Fig. 3**Fig. 4*

*Fig. 5**Fig. 6*

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ALLOY COMPOSITIONS FOR LITHIUM ION BATTERIES**RELATED APPLICATION**

This application claims priority from U.S. Provisional Application No. 60/702,241, which was filed on Jul. 25, 2005 and is hereby incorporated by reference.

FIELD OF INVENTION

Alloy compositions for lithium ion batteries are described.

BACKGROUND

Rechargeable lithium ion batteries are included in a variety of electronic devices. Most commercially available lithium ion batteries have anodes that contain materials such as graphite that are capable of incorporating lithium through an intercalation mechanism during charging. Such intercalation-type anodes generally exhibit good cycle life and coulombic efficiency. However, the amount of lithium that can be incorporated per unit mass of intercalation-type material is relatively low.

A second class of anode material is known that incorporates lithium through an alloying mechanism during charging. Although these alloy-type materials can often incorporate higher amounts of lithium per unit mass than intercalation-type materials, the addition of lithium to the alloy is usually accompanied with a large volume change. Some alloy-type anodes exhibit relatively poor cycle life and coulombic efficiency. The poor performance of these alloy-type anodes may result from the formation of a two-phase region during lithiation and delithiation. The two-phase region can create internal stress within the alloy if one phase undergoes a larger volume change than the other phase. This internal stress can lead to the disintegration of the anode material over time.

Further, the large volume change accompanying the incorporation of lithium can result in the deterioration of electrical contact between the alloy, conductive diluent (e.g., carbon) particles, and binder that typically form the anode. The deterioration of electrical contact, in turn, can result in diminished capacity over the cycle life of the anode.

SUMMARY

Alloy compositions, lithium ion batteries, and methods of making lithium ion batteries are described. More specifically, the lithium ion batteries have anodes that contain alloy compositions that are a mixture of an amorphous phase and a nanocrystalline phase.

In one aspect, a lithium ion battery is described that contains a cathode, an anode, and an electrolyte that is in electrical communication with both the anode and the cathode. The anode includes an alloy composition that contains (a) silicon in an amount of 35 to 70 mole percent, (b) aluminum in an amount of 1 to 45 mole percent, (c) a transition metal in an amount of 5 to 25 mole percent, (d) tin in an amount of 1 to 15 mole percent, and (e) a fifth element that includes yttrium, a lanthanide element, an actinide element, or a combination thereof in an amount of 2 to 15 mole percent. Each mole percent is based on a total number of moles of all elements except lithium in the alloy composition. The alloy composition is a mixture of an amorphous phase that includes silicon and a nanocrystalline phase that includes tin and the fifth element.

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In another aspect, a method of making a lithium ion battery is described that includes preparing an anode that contains an alloy composition, providing a cathode, and providing an electrolyte that is in electrical communication with both the anode and the cathode. The alloy composition contains (a) silicon in an amount of 35 to 70 mole percent, (b) aluminum in an amount of 1 to 45 mole percent, (c) a transition metal in an amount of 5 to 25 mole percent, (d) tin in an amount of 1 to 15 mole percent, and (e) a fifth element that includes yttrium, a lanthanide element, an actinide element, or a combination thereof in an amount of 2 to 15 mole percent. Each mole percent is based on a total number of moles of all elements except lithium in the alloy composition. The alloy composition is a mixture of an amorphous phase that includes silicon and a nanocrystalline phase that includes tin and the fifth element.

In yet another aspect, an alloy composition is described. The alloy composition contains (a) silicon in an amount of 35 to 70 mole percent, (b) aluminum in an amount of 1 to 45 mole percent, (c) a transition metal in an amount of 5 to 25 mole percent, (d) tin in an amount of 1 to 15 mole percent, and (e) a fifth element that includes yttrium, a lanthanide element, an actinide element, or a combination thereof in an amount of 2 to 15 mole percent. Each mole percent is based on a total number of moles of all elements except lithium in the alloy composition. The alloy composition is a mixture of an amorphous phase that includes silicon and a nanocrystalline phase that includes tin and the fifth element.

As used herein, the terms “a”, “an”, and “the” are used interchangeably with “at least one” to mean one or more of the elements being described.

The term “amorphous” refers to a material that lacks the long-range atomic order characteristic of crystalline material, as determined using x-ray diffraction techniques.

The terms “crystalline”, “crystallite”, and “crystals” refer to materials that have long-range order as determined using x-ray diffraction techniques. The crystalline materials have a maximum dimension of at least about 5 nanometers. The terms “nanocrystalline”, “nanocrystallite”, and “nanocrystals” refer to a subset of crystalline materials that have a maximum dimension of about 5 to about 50 nanometers. Some crystalline materials are larger than nanocrystalline materials (i.e., some have a maximum dimension larger than about 50 nanometers).

The term “electrochemically active” refers to a material that reacts with lithium under conditions typically encountered during charging of a lithium ion battery. The electrochemically active material is usually in the form of a metal or alloy.

The term “electrochemically inactive” refers to a material that does not react with lithium under conditions typically encountered during charging of a lithium ion battery. The electrochemically inactive material is usually in the form of a metal or alloy.

The term “metal” refers to both metals and metalloids such as silicon and germanium. The metal is often in an elemental state. An “intermetallic” compound is a compound that includes at least two metals.

The term “lithiation” refers to the process of adding lithium to the alloy composition (i.e., lithium ions are reduced).

The term “delithiation” refers to the process of removing lithium from the alloy composition (i.e., lithium atoms are oxidized).

The term “charging” refers to a process of providing electrical energy to a battery.

The term “discharging” refers to a process of removing electrical energy from a battery (i.e., discharging is a process of using the battery to do useful work).

The term “capacity” refers to the amount of lithium that can be incorporated into the anode material (e.g., the alloy composition) and has units of milliamp-hours (mAh). The term “specific capacity” refers to the capacity per unit mass of the anode material and has units of milliamp-hour/gram (mAh/g).

The term “cathode” refers to the electrode where electrochemical reduction occurs during the discharging process. During discharging, the cathode undergoes lithiation. During charging, lithium atoms are removed from this electrode.

The term “anode” refers to the electrode where electrochemical oxidation occurs during the discharging process. During discharging, the anode undergoes delithiation. During charging, lithium atoms are added to this electrode.

As used herein, a “number in the range of” includes the endpoints of the range and all the numbers between the endpoints. For example, a number in the range of 1 to 10 includes 1, 10, and all the numbers between 1 and 10.

The above summary is not intended to describe each disclosed embodiment or every implementation of the present invention. The detailed description section that follows more particularly exemplifies these embodiments.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention can be more completely understood in consideration of the following detailed description of various embodiments of the invention in connection with the accompanying drawings, in which:

FIG. 1 is the x-ray diffraction pattern of an exemplary alloy composition $\text{Si}_{60}\text{Al}_{14}\text{Fe}_8\text{Ti}_1\text{Sn}_7(\text{MM})_{10}$ where MM refers to mischmetal.

FIG. 2 is a plot of voltage versus capacity of an electrochemical cell having an electrode that contains the alloy composition $\text{Si}_{60}\text{Al}_{14}\text{Fe}_8\text{Ti}_1\text{Sn}_7(\text{MM})_{10}$.

FIG. 3 is the x-ray diffraction pattern of an exemplary alloy composition $\text{Si}_{60}\text{Al}_{12}\text{Fe}_8\text{Ti}_3\text{Sn}_7(\text{MM})_{10}$.

FIG. 4 is the x-ray diffraction pattern of an exemplary alloy composition $\text{Si}_{60}\text{Al}_{15}\text{Fe}_8\text{Sn}_7(\text{MM})_{10}$.

FIG. 5 is the x-ray diffraction pattern of an exemplary alloy composition $\text{Si}_{41.4}\text{Al}_{39.5}\text{CO}_{13.1}\text{Sn}_2(\text{MM})_4$.

FIG. 6 is a plot of voltage versus capacity of an electrochemical cell having an electrode that contains lithium powder and the alloy composition $\text{Si}_{60}\text{Al}_{14}\text{Fe}_8\text{Ti}_1\text{Sn}_7(\text{MM})_{10}$.

While the invention is amenable to various modifications and alternative forms, specifics thereof have been shown by way of example in the drawings and will be described in detail. It should be understood, however, that the intention is not to limit the invention to the particular embodiments described. On the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention.

DETAILED DESCRIPTION

Alloy compositions are described that can be included in the anode of a lithium ion battery. The alloy compositions are a mixture of an amorphous phase and a nanocrystalline phase. Compared to materials that contain large crystallites (i.e., crystals having a maximum dimension greater than about 50 nanometers), this mixture can advantageously decrease the risk of anode disintegration over time due to internal stress. Additionally, compared to materials that are entirely amorphous, this mixture can advantageously result in anodes hav-

ing an increased rate of lithiation. Anodes having an increased rate of lithiation can be recharged at a faster rate.

In one aspect, lithium ion batteries are provided that include a cathode, an anode, and an electrolyte that is in electrical communication with both the cathode and the anode. The alloy composition contains (a) silicon, (b) aluminum, (c) a transition metal, (d) tin, and (e) a fifth element that includes yttrium, a lanthanide element, an actinide element, or a combination thereof. The amorphous phase contains silicon while the nanocrystalline phase is substantially free of silicon. The nanocrystalline phase contains an intermetallic compound that includes tin and the fifth element.

The amorphous nature of the alloy compositions can be characterized by the absence of sharp peaks in the x-ray diffraction pattern. The x-ray diffraction pattern can have broad peaks, such as peaks having a peak width at half the maximum peak height corresponding to at least 5 degrees two theta, at least 10 degrees two theta, or at least 15 degrees two theta using a copper target (i.e., copper K α 1 line, copper K α 2 line, or a combination thereof).

Nanocrystalline materials typically have a maximum dimension of about 5 nanometers to about 50 nanometers. The crystalline size can be determined from the width of an x-ray diffraction peak using the Scherrer equation. Narrower x-ray diffraction peaks correspond to larger crystal sizes. The x-ray diffraction peaks for nanocrystalline materials typically have a peak width at half the maximum peak height corresponding to less than 5 degrees two theta, less than 4 degrees two theta, less than 3 degrees two theta, less than 2 degrees two theta, or less than 1 degree two theta using a copper target (i.e., copper K α 1 line, copper K α 2 line, or a combination thereof). The nanocrystalline material has a peak width at half of the maximum peak height corresponding to at least 0.2 degrees two theta, at least 0.5 degrees two theta, or at least 1 degree two theta using a copper target.

Because the rate of lithiation is generally greater for nanocrystalline material than for amorphous material, it is desirable to include some nanocrystalline material in the alloy composition. The presence of elemental silicon in a crystalline phase, however, can result in the formation of crystalline $\text{Li}_{15}\text{Si}_4$ during cycling when the voltage drops below about 50 mV versus a metallic Li/Li ion reference electrode. The formation of crystalline $\text{Li}_{15}\text{Si}_4$ during lithiation can adversely affect the cycle life of the anode (i.e., the capacity tends to diminish with each cycle of lithiation and delithiation). To minimize or prevent the formation of $\text{Li}_{15}\text{Si}_4$ crystals, it is advantageous for silicon to be present in the amorphous phase and to remain in the amorphous phase after repetitive cycles of lithiation and delithiation. The addition of a transition metal facilitates the formation of an amorphous silicon-containing phase and minimizes or prevents the formation of a crystalline silicon-containing phase (e.g., crystalline elemental silicon or crystalline silicon-containing compounds).

The nanocrystalline phase of the alloy composition includes tin, which is another electroactive material, rather than silicon. The presence of crystalline elemental tin, however, can be detrimental to the capacity when the anode is subjected to repetitive cycles of lithiation and delithiation. As used herein, the term “elemental” refers to an element of the periodic table (e.g., tin or silicon) that is present in an elemental form (i.e., as a pure element) rather than combined with another element in the form of a compound such as an intermetallic compound.

To minimize the formation of crystalline elemental tin, a fifth element that includes yttrium, a lanthanide element, an actinide element, or a combination thereof is added to the alloy composition. The fifth element forms an intermetallic

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compound with tin that is often of formula Sn_3M where M is selected from yttrium, a lanthanide element, an actinide element, or a combination thereof. In the absence of the fifth element in the alloy composition, it can be difficult to control the size of the crystalline phase using some formation processes. For example, when an alloy is formed using a melt spinning technique without any of the fifth element, relatively large crystals of elemental tin can form.

The alloy composition includes an amorphous phase that includes all of the silicon. The amorphous phase typically includes all or a portion of the aluminum and all or a portion of the transition metal. The alloy further includes a nanocrystalline phase that includes an intermetallic compound of tin with the fifth element. The nanocrystalline phase can include all or a portion of the tin and all or a portion of the fifth element. The nanocrystalline phase is substantially free of silicon. That is, the nanocrystalline phase is substantially free of elemental silicon and substantially free of a silicon-containing stoichiometric compound such as a silicide. Further, the nanocrystalline phase is substantially free of elemental tin. As used herein, the term "substantially free" when referring to the nanocrystalline phase means that the substances (e.g., elemental silicon, a silicon-containing compound, or elemental tin) cannot be detected using x-ray diffraction techniques.

The specific capacity (i.e., the capacity per gram) of the alloy compositions is usually at least 200 mAh/g. In some embodiments, the specific capacity can be at least 400 mAh/g, at least 600 mAh/g, at least 800 mAh/g, at least 1000 mAh/g, at least 1200 mAh/g, at least 1600 mAh/g, at least 1800 mAh/g, or at least 2000 mAh/g. The specific capacity is typically measured during the discharging portion of the second cycle of lithiation and delithiation.

As used herein, the term "mole percent" when referring to constituents of the alloy composition is calculated based on the total number of moles of all elements in the alloy composition except lithium. For example, the mole percent silicon in an alloy that contains silicon, aluminum, transition metal, tin, and a fifth element is calculated by multiplying the moles of silicon by 100 and dividing this product by the total moles of all elements except lithium in the alloy composition (e.g., moles of silicon+moles of aluminum+moles of transition metal+moles of tin+moles of fifth element).

All of the silicon is generally in the amorphous phase. Silicon is present in the alloy composition in an amount of 35 to 70 mole percent based on the total number of moles of all elements except lithium in the alloy composition. If the amount of silicon is too low, the capacity can be unacceptably low. If the amount of silicon is too high, however, silicon-containing crystals tend to form. The presence of crystalline silicon, at least in some embodiments, can lead to the formation of $\text{Li}_{15}\text{Si}_4$ during cycling when the voltage drops below about 50 mV versus a metallic Li/Li ion reference electrode. Crystalline $\text{Li}_{15}\text{Si}_4$ can detrimentally affect the cycle life of a lithium ion battery.

The alloy composition contains at least 35 mole percent, at least 40 mole percent, at least 45 mole percent, at least 50 mole percent, at least 55 mole percent, or at least 60 mole percent silicon. The alloy composition can contain up to 70 mole percent, up to 65 mole percent, or up to 60 mole percent silicon. For example, the alloy composition can contain 40 to 70 mole percent, 40 to 65 mole percent, 35 to 55 mole percent, 50 to 70 mole percent, 55 to 70 mole percent, or 55 to 65 mole percent silicon.

Aluminum is another element that is present in the alloy composition. The aluminum is typically present in the amorphous phase and, along with the transition metal, facilitates

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the formation of the amorphous phase that contains all of the silicon. The aluminum can be electrochemically active, electrochemically inactive, or a combination thereof. If the aluminum is present as elemental aluminum, it is often electrochemically active. Electrochemically active aluminum can enhance the capacity of the alloy composition. If the aluminum is present as an intermetallic compound with a transition metal, however, it can be electrochemically inactive. As an electrochemically inactive material, an aluminum intermetallic compound can function as a matrix for the electrochemically active components.

Aluminum is present in the alloy composition in an amount of 1 to 45 mole percent based on the total number of the moles of all elements except lithium in the alloy composition. The addition of aluminum to the alloy composition often lowers the melting point, which can facilitate the use of melt processing technique such as melt spinning. Melt processing techniques are often less expensive than processing techniques such as sputtering to form an alloy composition. If the aluminum level is too low, it can be more difficult to form an amorphous phase that contains all of the silicon. Too much aluminum, however, can detrimentally affect the cycle life of the lithium ion battery. That is, too much aluminum can result in an unacceptably large capacity decrease when the anode is subjected to repetitive cycles of lithiation and delithiation.

The alloy composition contains up to 45 mole percent, up to 40 mole percent, up to 35 mole percent, up to 30 mole percent, up to 25 mole percent, up to 20 mole percent, or up to 15 mole percent aluminum. The aluminum in the alloy composition is often present in an amount of at least 1 mole percent, at least 2 mole percent, at least 5 mole percent, at least 10 mole percent, at least 20 mole percent, or at least 25 mole percent. For example, the alloy composition can contain 2 to 40 mole percent, 3 to 40 mole percent, 5 to 40 mole percent, 10 to 40 mole percent, 10 to 30 mole percent, 1 to 25 mole percent, 25 to 45 mole percent, or 10 to 20 mole percent aluminum.

The alloy composition also includes a transition metal in an amount of 5 to 25 mole percent based on a total number of moles of all elements except lithium in the alloy composition. Suitable transition metals include, but are not limited to, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zirconium, niobium, molybdenum, tungsten, and combinations thereof. The transition metal, in combination with aluminum, facilitates the formation of the amorphous phase. If too little transition metal is included in the alloy composition, it can be more difficult to form an amorphous phase that includes all of the silicon. If the transition metal concentration is too high, however, the capacity of the alloy composition can be unacceptably low because the transition metal is electrochemically inactive or combines with another component such as aluminum to form an intermetallic compound that is electrochemically inactive.

The transition element is present in an amount of at least 5 mole percent, at least 8 mole percent, at least 10 mole percent, or at least 12 mole percent. The alloy composition contains up to 25 mole percent, up to 20 mole percent, or up to 15 mole percent transition metal. For example, the alloy composition includes 5 to 20 mole percent, 5 to 15 mole percent, 8 to 25 mole percent, 8 to 20 mole percent, or 10 to 25 mole percent transition metal.

Tin is yet another element present in the alloy composition. Tin is typically present in the nanocrystalline phase as an intermetallic compound with a fifth element containing yttrium, a lanthanide element, an actinide element, or a combination thereof. The intermetallic compound is often of formula Sn_3M where M is the fifth element. The nanocrystalline

phase can increase the rate of lithiation of the alloy composition, particularly during the first cycle of lithiation and delithiation. Although not wanting to be bound by theory, the nanocrystalline phase may be analogous to veins through the amorphous phase. The nanocrystalline phase may provide a conduction path for lithium throughout the alloy composition, which may allow lithium to diffuse quickly along the grain boundaries between the nanocrystalline phase and the amorphous phase.

The alloy composition contains 1 to 15 mole percent tin based on the total number of moles of all elements except lithium in the alloy composition. If too much tin is present, crystalline tin can form rather than a nanocrystalline tin-containing, intermetallic compound. Crystalline elemental tin detrimentally affects the capacity when the anode is subjected to repetitive cycles of lithiation and delithiation. That is, too much tin can cause the capacity to decrease unacceptably when the anode is subjected to repetitive cycles of lithiation and delithiation. If the amount of tin is too low, however, the rate of lithiation may be comparable to that of an amorphous material.

Tin is present in an amount up to 15 mole percent, up to 12 mole percent, up to 10 mole percent, up to 9 mole percent, up to 8 mole percent, up to 7 mole percent, up to 6 mole percent, or up to 5 mole percent. Tin is usually present in an amount of at least 1 mole percent, at least 2 mole percent, at least 3 mole percent, at least 4 mole percent, or at least 5 mole percent. For example, the alloy composition can contain 1 to 12 mole percent, 1 to 10 mole percent, 1 to 9 mole percent, 2 to 9 mole percent, 2 to 8 mole percent, or 3 to 9 mole percent tin.

A fifth element is included in the alloy composition that contains yttrium, a lanthanide element, an actinide element, or a combination thereof in an amount of 2 to 15 mole percent based on the total number of moles of all elements except lithium in the alloy composition. The fifth element is included in the nanocrystalline phase in the form of an intermetallic compound with tin. If the alloy composition contains too much of the fifth element, the capacity can be reduced because the fifth element is typically electrochemically inactive. On the other hand, if the amount of the fifth element is too low, there can be some tin that is in the form of crystalline elemental tin rather than in the form of a nanocrystalline tin-containing, intermetallic compound. The presence of crystalline elemental tin can deleteriously affect the capacity when the lithium ion battery is subjected to repetitive cycles of lithiation and delithiation.

The nanocrystalline phase is substantially free of a stoichiometric compound such as a silicide formed by combining silicon with the fifth element. A stoichiometric compound has a defined ratio between the elements in the compound with the ratio being a rational number.

Suitable lanthanide elements include lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. Suitable actinide elements include thorium, actinium, and protactinium. Some alloy compositions contain a lanthanide elements selected, for example, from cerium, lanthanum, praseodymium, neodymium, or a combination thereof.

The fifth element can be a mischmetal, which is an alloy of various lanthanides. Some mischmetals contain, for example, 45 to 60 weight percent cerium, 20 to 45 weight percent lanthanum, 1 to 10 weight percent praseodymium, and 1 to 25 weight percent neodymium. Other mischmetals contains 30 to 40 weight percent lanthanum, 60 to 70 weight percent cerium, less than 1 weight percent praseodymium, and less than 1 weight percent neodymium. Still other mischmetals

contains 40 to 60 weight percent cerium and 40 to 60 weight percent lanthanum. The mischmetal often includes small impurities (e.g., less than 1 weight percent, less than 0.5 weight percent, or less than 0.1 weight percent) such as, for example, iron, magnesium, silicon, molybdenum, zinc, calcium, copper, chromium, lead, titanium, manganese, carbon, sulfur, and phosphorous. The mischmetal often has a lanthanide content of at least 97 weight percent, at least 98 weight percent, or at least 99 weight percent. One exemplary mischmetal that is commercially available from Alfa Aesar, Ward Hill, Mass. with 99.9 weight percent purity contains approximately 50 weight percent cerium, 18 weight percent neodymium, 6 weight percent praseodymium, 22 weight percent lanthanum, and 3 weight percent other rare earths.

The alloy composition contains at least 2 mole percent, at least 3 mole percent, or at least 5 mole percent of the fifth element. The fifth element can be present in amounts up to 15 mole percent, up to 12 mole percent, or up to 10 mole percent in the alloy composition. For example, the alloy composition can contain 3 to 15 mole percent, 5 to 15 mole percent, 3 to 12 mole percent, or 3 to 10 mole percent of the fifth element. In some embodiments, the fifth element is a lanthanide element or a mixture of lanthanide elements.

The alloy composition is substantially free of an alkaline earth metal such as calcium, barium, magnesium, and the like. As used herein, the term "substantially free" with reference to an alkaline earth metal means that the alloy composition contains no more than 1 mole percent alkaline earth, no more than 0.5 mole percent alkaline earth, no more than 0.2 mole percent alkaline earth, or no more than 0.1 mole percent alkaline earth. An alkaline earth, if present in the alloy composition, is typically present as an impurity of another component and is not purposefully added.

The alloy composition can further include an alkali metal such as lithium. Prior to the first lithiation reaction, the alloy composition typically contains little or no lithium. After the first lithiation, the amount of lithium can vary but is typically greater than zero even after the lithium ion battery has been discharged. That is, the anode containing the alloy composition often has at least a small amount of irreversible capacity.

The alloy compositions are often of Formula I



where a is a number in the range of 35 to 70; b is a number in the range of 1 to 45; T is a transition metal; c is a number in the range of 5 to 25; d is a number in the range of 1 to 15; M is yttrium, a lanthanide element, an actinide element, or a combination thereof; e is a number in the range of 2 to 15; and the sum of a+b+c+d+e is equal to 100. The variable f can range from 0 to a number equal to $[4.4(a+d)+b]$.

In some exemplary compositions according to Formula I, the variable a is a number in the range of 40 to 65; b is a number in the range of 1 to 25; c is a number in the range of 5 to 25; d is a number in the range of 1 to 15; and e is a number in the range of 2 to 15. In other exemplary compositions according to Formula I, the variable a is a number in the range of 35 to 55; b is a number in the range of 25 to 45; c is a number in the range of 5 to 25; d is a number in the range of 1 to 15; and e is a number in the range of 2 to 15. In still other exemplary compositions, the variable a is a number in the range of 55 to 65; b is a number in the range of 10 to 20; c is a number in the range of 5 to 25; d is a number in the range of 1 to 15; and e is a number in the range of 2 to 15.

The alloy composition of the anode can be in the form of a thin film or powder, the form depending on the technique chosen to prepare the materials. Suitable methods of prepar-

ing the alloy compositions include, but are not limited to, sputtering, chemical vapor deposition, vacuum evaporation, melt processing such as melt spinning, splat cooling, spray atomization, electrochemical deposition, and ball milling.

The method of making the alloy composition can involve forming an amorphous material and then annealing the amorphous material at a temperature in the range of about 150° C. to about 400° C. Annealing tends to convert a precursor material that is entirely amorphous into an alloy composition that is a mixture of an amorphous phase and a nanocrystalline phase. The annealing step is typically conducted by heating the precursor material in an inert environment such as argon or helium.

Sputtering is one method for producing amorphous precursor. The different elements can be sputtered simultaneously or sequentially. For example, the elements can be sequentially sputter-coated on a substrate such as a copper substrate. The substrates can be positioned near the edge of a turntable (e.g., 25 inch diameter) that rotates continuously below multiple sputtering sources that are operating continuously. A layer of one material can be deposited as the substrate passes under the first sputtering source, and additional layers of different material can be deposited as the substrate passes under the other sputtering sources. The amount of material deposited from each sputtering source can be controlled by varying the rotation speed of the turntable and by varying the sputtering rates. Suitable sputtering methods are further described in U.S. Pat. No. 6,203,944 B1 (Turner et al.); U.S. Pat. No. 6,436,578 B1 (Turner et al.); and U.S. Pat. No. 6,699,336 B2 (Turner et al.), all of which are incorporated herein by reference.

Melt processing is another procedure that can be used to produce amorphous precursors or for producing alloy compositions that are a mixture of amorphous materials and nanocrystalline materials. Such processes are described generally, for example, in *Amorphous Metallic Alloys*, F. E. Luborsky, ed., Chapter 2, Butterworth & Co., Ltd., 1983. Ingots containing the reactants can be melted in a radio frequency field and then ejected through a nozzle onto a surface of a rotating wheel (e.g., a copper alloy wheel) that can be cooled. Because the surface temperature of the rotating wheel is substantially lower than the temperature of the melt, contact with the surface of the rotating wheel quenches the melt. Rapid quenching minimizes the formation of crystalline material and favors the formation of amorphous materials. Suitable melt processing methods are further described in U.S. Pat. No. 6,699,336 B2 (Turner et al.), incorporated herein by reference. The melt-processed material can be in the form, for example, of a ribbon or thin film.

In some melt processing procedures, depending on the quenching rate and the particular material, the resulting material can be a mixture of an amorphous phase and a single nanocrystalline phase that includes an intermetallic compound of tin, indium, and the sixth element. In other melt processing procedures, however, the melt-processed material is a precursor that contains (1) an amorphous phase, (2) a ternary nanocrystalline phase that includes an intermetallic compound of tin, indium and the sixth element, and (3) a crystalline (e.g., nanocrystalline) elemental tin phase, a crystalline indium phase, a crystalline binary tin-indium phase of formula $\text{Sn}_{(1-y)}\text{In}_y$, where y is a positive number less than 1 such as, for example, $\text{Sn}_{0.8}\text{In}_{0.2}$, or a combination thereof. The crystalline elemental tin phase, crystalline indium phase, and the crystalline binary tin-indium phase can often be removed by annealing the melt-processed material at a temperature in the range of about 150° C. to about 400° C. under an inert atmosphere. In still other melt processing methods,

the melt-processed precursor material is a precursor that contains only amorphous materials. The precursor can be annealed at a temperature in the range of about 150° C. to about 400° C. under an inert atmosphere to prepare the alloy composition that contains both an amorphous phase and a nanocrystalline phase.

The sputtered or melt processed alloy compositions can be further treated to produce powdered materials. For example, a ribbon or thin film of the alloy composition can be pulverized to form a powder. The powder can be formed before or after any annealing step. Exemplary powders have a maximum dimension that is no greater than 60 micrometers, no greater than 40 micrometers, or no greater than 20 micrometers. The powders often have a maximum dimension of at least 1 micrometer, at least 2 micrometers, at least 5 micrometers, or at least 10 micrometers. For example, suitable powders often have a maximum dimension of 1 to 60 micrometers, 10 to 60 micrometers, 20 to 60 micrometers, 40 to 60 micrometers, 1 to 40 micrometers, 2 to 40 micrometers, 10 to 40 micrometers, 5 to 20 micrometers, or 10 to 20 micrometers.

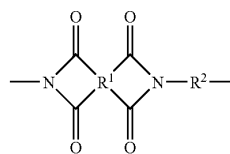
In some embodiments, the anode contains the alloy composition dispersed in an elastomeric polymer binder. Exemplary elastomeric polymer binders include polyolefins such as those prepared from ethylene, propylene, or butylene monomers; fluorinated polyolefins such as those prepared from vinylidene fluoride monomers; perfluorinated polyolefins such as those prepared from hexafluoropropylene monomer; perfluorinated poly(alkyl vinyl ethers); perfluorinated poly(alkoxy vinyl ethers); or

combinations thereof. Specific examples of elastomeric polymer binders include terpolymers of vinylidene fluoride, tetrafluoroethylene, and propylene; and copolymers of vinylidene fluoride and hexafluoropropylene. Commercially available fluorinated elastomers include those sold by Dyneon, LLC, Oakdale, Minn. under the trade designation "FC-2178", "FC-2179", and "BRE-7131X".

In some anodes, the elastomeric binders are crosslinked. Crosslinking can improve the mechanical properties of the polymer and can improve the contact between the alloy composition and any electrically conductive diluent that may be present.

In other anodes, the binder is a polyimide such as the aliphatic or cycloaliphatic polyimides described in U.S. patent application Ser. No. 11/218,448 filed on Sep. 1, 2005. Such polyimide binders have repeating units of Formula II

II



where R^1 is aliphatic or cycloaliphatic; and R^2 is aromatic, aliphatic, or cycloaliphatic.

The aliphatic or cycloaliphatic polyimide binders may be formed, for example, using a condensation reaction between an aliphatic or cycloaliphatic polyanhydride (e.g., a dianhydride) and an aromatic, aliphatic or cycloaliphatic polyamine (e.g., a diamine or triamine) to form a polyamic acid, followed by chemical or thermal cyclization to form the polyimide. The polyimide binders may also be formed using reaction mixtures additionally containing aromatic

polyanhydrides (e.g., aromatic dianhydrides), or from reaction mixtures containing copolymers derived from aromatic polyanhydrides (e.g., aromatic dianhydrides) and aliphatic or cycloaliphatic polyanhydrides (e.g., aliphatic or cycloaliphatic dianhydrides). For example, about 10 to about 90 percent of the imide groups in the polyimide may be bonded to aliphatic or cycloaliphatic moieties and about 90 to about 10 percent of the imide groups may be bonded to aromatic moieties. Representative aromatic polyanhydrides are described, for example, in U.S. Pat. No. 5,504,128 (Mizutani et al.).

An electrically conductive diluent can be mixed with the alloy composition in the anode. Exemplary electrically conductive diluents include, but are not limited to, carbon, metal, metal nitrides, metal carbides, metal silicides, and metal borides. In some anodes, the electrically conductive diluents are carbon blacks such as those commercially available from MMM Carbon of Belgium under the trade designation "SUPER P" and "SUPER S" or from Chevron Chemical Co. of Houston, Tex. under the trade designation "SHAWINIGAN BLACK"; acetylene black; furnace black; lamp black; graphite; carbon fibers; or combinations thereof.

The anode can further include an adhesion promoter that promotes adhesion of the alloy composition and the electrically conductive diluent to the elastomeric polymer binder. The combination of an adhesion promoter and elastomeric polymer binder accommodates, at least partially, volume changes that may occur in the alloy composition during repeated cycles of lithiation and delithiation. The adhesion promoter can be part of the binder (e.g., in the form of a functional group) or can be in the form of a coating on the alloy composition, the electrically conductive diluent, or a combination thereof. Examples of adhesion promoters include, but are not limited to, silanes, titanates, and phosphonates as described in U.S. Pat. No. 7,341,804, the disclosure of which is incorporated herein by reference.

The anode can be partially lithiated prior to or during the battery assembly process. Adding lithium to the anode can increase the energy delivered by the battery during discharging. In some embodiments, the anode is partially lithiated by dispersing a lithium powder, the alloy composition, and a conductive diluent in a solution of a polymer binder. The dispersion can be coated, dried to remove any solvent, and cured to form the electrode. In other embodiments, lithium foil or a lithium metal powder can be added to the surface of a previously cured electrode. In the case of a lithium metal powder, the powder can be distributed 1) by sprinkling the powder directly onto the surface of the electrode or 2) by dispersing the lithium metal powder in a volatile solvent that is non-reactive, followed by evenly coating the lithium dispersion onto the electrode surface and evaporating off the solvent. The lithium foil or lithium metal powder can then be affixed to the electrode by a calendaring process. Although anodes that contain lithium can be heated before battery assembly to react the lithium with the other components of the anode, such anodes are typically assembled into batteries without heating. During the battery assembly process, the lithium can react with the other components of the anode coating when electrolyte is added.

Any suitable electrolyte can be included in the lithium ion battery. The electrolyte can be in the form of a solid or liquid. Exemplary solid electrolytes include polymeric electrolytes such as polyethylene oxide, polytetrafluoroethylene, polyvinylidene fluoride, fluorine-containing copolymers, polyacrylonitrile, or combinations thereof. Exemplary liquid electrolytes include ethylene carbonate, dimethyl carbonate, diethyl carbonate, propylene carbonate, gamma-butyrolactone, tetra-

rahydrofuran, 1,2-dimethoxyethane, dioxolane, 4-fluoro-1,3-dioxolan-2-one, or combinations thereof. The electrolyte includes a lithium electrolyte salt such as LiPF_6 , LiBF_4 , LiClO_4 , $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, $\text{LiN}(\text{SO}_2\text{CF}_2\text{CF}_3)_2$, and the like.

The electrolyte can include a redox shuttle molecule, an electrochemically reversible material that during charging can become oxidized at the cathode, migrate to the anode where it can become reduced to reform the unoxidized (or less-oxidized) shuttle species, and migrate back to the cathode. Exemplary redox shuttle molecules include those described in U.S. Pat. No. 5,709,968 (Shimizu), U.S. Pat. No. 5,763,119 (Adachi), U.S. Pat. No. 5,536,599 (Alamgir et al.), U.S. Pat. No. 5,858,573 (Abraham et al.), U.S. Pat. No. 5,882,812 (Visco et al.), U.S. Pat. No. 6,004,698 (Richardson et al.), U.S. Pat. No. 6,045,952 (Kerr et al.), and U.S. Pat. No. 6,387,571 B1 (Lain et al.); PCT Published Patent Application No. WO 01/29920 A1 (Richardson et al.); and in U.S. Patent Publication No. 2005-0221196 (Dahn et al.); and U.S. Pat. No. 7,615,312 (Dahn et al.) and U.S. Pat. No. 7,615,317 (Dahn et al.); and U.S. Provisional Patent Application Ser. No. 60/743,314 filed on Feb. 17, 2006 (Dahn et al.).

Any suitable cathode known for use in lithium ion batteries can be utilized. Some exemplary cathodes contain lithium transition metal oxide such as lithium cobalt dioxide, lithium nickel dioxide, and lithium manganese dioxide. Other exemplary cathodes are disclosed in U.S. Pat. No. 6,680,145 B2 (Obrovac et al.), incorporated herein by reference, and include transition metal grains in combination with lithium-containing grains. Suitable transition metal grains include, for example, iron, cobalt, chromium, nickel, vanadium, manganese, copper, zinc, zirconium, molybdenum, niobium, or combinations thereof with a grain size no greater than about 50 nanometers. Suitable lithium-containing grains can be selected from lithium oxides, lithium sulfides, lithium halides (e.g., chlorides, bromides, iodides, or fluorides), or combinations thereof. These particles can be used alone or in combination with a lithium-transition metal oxide material such as lithium cobalt dioxide.

In some lithium ion batteries with solid electrolytes, the cathode can include LiV_3O_8 or LiV_2O_5 . In other lithium ion batteries with liquid electrolytes, the cathode can include LiCoO_2 , $\text{LiCO}_{0.2}\text{Ni}_{0.8}\text{O}_2$, LiMn_2O_4 , LiFePO_4 , or LiNiO_2 .

The lithium ion batteries can be used as a power supply in a variety of applications. For example, the lithium ion batteries can be used in power supplies for electronic devices such as computers and various hand-held devices, motor vehicles, power tools, photographic equipment, and telecommunication devices. Multiple lithium ion batteries can be combined to provide a battery pack.

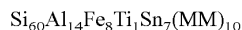
EXAMPLES

Aluminum, silicon, iron, titanium, tin, zirconium, and cobalt were obtained as pure elements in high purity (99.8 weight percent or greater) from Alfa Aesar, Ward Hill, Mass. or Aldrich, Milwaukee, Wis. A mixture of rare earth elements, also known as mischmetal (MM), was also obtained from Alfa Aesar with 99.0 weight percent minimum rare earth content which contained approximately 50 weight percent cerium, 18 weight percent neodymium, 6 weight percent praseodymium, 22 weight percent lanthanum, and 4 weight percent other rare earth elements.

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The alloy compositions were formed into electrodes and characterized in electrochemical cells using a lithium metal counter electrode.

Example 1



An alloy composition $\text{Si}_{60}\text{Al}_{14}\text{Fe}_8\text{Ti}_1\text{Sn}_7(\text{MM})_{10}$ was prepared by melting a mixture of 7.89 g aluminum shot, 35.18 g silicon flakes, 9.34 g iron shot, 1.00 g titanium granules, 17.35 g tin shot, and 29.26 g mischmetal (MM) in an in an argon-filled arc furnace (commercially available from Advanced Vacuum Systems, Ayer, Mass.) with a copper hearth to produce an ingot. The ingot was cut into strips using a diamond blade wet saw.

The ingots were then further processed by melt spinning. The melt spinning apparatus included a vacuum chamber having a cylindrical quartz glass crucible (16 mm internal diameter and 140 mm length) with a 0.35 mm orifice that was positioned above a rotating cooling wheel. The rotating cooling wheel (10 mm thick and 203 mm diameter) was fabricated from a copper alloy (Ni—Si—Cr—Cu C18000 alloy, 0.45 weight percent chromium, 2.4 weight percent nickel, 0.6 weight percent silicon with the balance being copper) that is commercially available from Nonferrous Products, Inc., Franklin, Ind. Prior to processing, the edge surface of the cooling wheel was polished using with a rubbing compound (commercially available from 3M, St. Paul, Minn. under the trade designation IMPERIAL MICROFINISHING) and then wiped with mineral oil to leave a thin film.

After placing a 20 g ingot strip in the crucible, the system was evacuated to 80 mT (milliTorr) and then filled with helium gas to 200 T. The ingot was melted using radio frequency induction. As the temperature reached 1350° C., 400 T helium pressure was applied to the surface of the molten alloy composition and the alloy composition was extruded through a nozzle onto the spinning (5031 revolutions per minute) cooling wheel. Ribbon strips were formed that had a width of 1 mm and a thickness of 10 micrometers. The ribbon strips were annealed at 200° C. for 2.5 hours under an argon atmosphere in a tube furnace.

The x-ray diffraction (XRD) pattern, obtained using a copper target ($\text{K}\alpha_1$, $\text{K}\alpha_2$ lines), is shown in FIG. 1 for the resulting alloy composition. The theoretical peak location for nanocrystalline $\text{Sn}_3(\text{MM})$ and crystalline Sn are superimposed on the XRD pattern. The sample contained nanocrystalline $\text{Sn}_3(\text{MM})$ but was substantially free of crystalline elemental tin. The XRD pattern did not contain any peaks associated with silicon. Thus, silicon was not in a crystalline phase but in the amorphous phase.

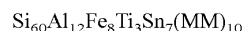
The following components were added to a 40 ml tungsten carbide milling vessel containing two 10 mm diameter and ten 3 mm diameter tungsten carbide balls: 1.60 g of the above ribbon, 240 mg of carbon (commercially available from MMM Carbon, Belgium under the trade designation SUPER P), 0.80 g of a polyimide coating solution (commercially available from HD Microsystems, Cheesapeake Rd, Parlin, N.J. under the trade designation PYRALIN PI2555 as a 20 weight percent solution in N-methyl-2-pyrrolidinone), and 5.2 g N-methyl-2-pyrroline (commercially available from Aldrich, Milwaukee, Wis.). The milling vessel was placed in a planetary mill (PULVERISETTE 7, available from Fritsch GmbH, Idon-Oberstein, Germany) and the contents were milled at a setting of “4” for one hour.

After milling, the mixture was transferred to a notched coating bar and coated onto a 15 micrometer thick copper foil

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as a strip having a width of 25 mm and a thickness of 125 micrometers. The strips were cured at 150° C. under vacuum conditions for 2.5 hours to form an electrode. The electrode was then used to construct 2325 coin cells having a 300 micrometer thick metallic lithium foil counter/reference electrode, two layers of a flat sheet polypropylene membrane separator (CELGARD 2400, commercially available from CELGARD Inc., Charlotte, N.C.), and 1 M LiPF_6 in a 1:2 mixture of ethylene carbonate and diethyl carbonate as the electrolyte. The 2325 coin cell hardware is described in A. M. Wilson and J. R. Dahn, *J Electrochem. Soc.*, 142, 326-332 (1995). The resulting voltage curve is illustrated by FIG. 2. The capacity was 800 mAh/g.

Example 2



An alloy composition $\text{Si}_{60}\text{Al}_{12}\text{Fe}_8\text{Ti}_3\text{Sn}_7(\text{MM})_{10}$ was prepared using a procedure similar to that of Example 1 by mixing 6.701 g of aluminum, 34.878 g silicon, 2.974 g titanium, 9.247 g iron, 17.197 g tin, and 29.002 g mischmetal. The XRD pattern of the resulting alloy composition is shown in FIG. 3.

An anode was prepared and tested as described in Example 1 except that the following components were mixed: 1.60 g of the extruded ribbon, 200 mg SUPER P carbon, and 1.00 g polyimide coating solution. The capacity was 700 mAh/g.

Example 3



An alloy composition $\text{Si}_{60}\text{Al}_{15}\text{Fe}_8\text{Sn}_7(\text{MM})_{10}$ was prepared using a procedure similar to that of Example 1 by mixing 8.487 g of aluminum, 35.337 g silicon, 9.369 g iron, 17.423 g tin, and 29.384 g mischmetal. The melt-spun sample was not annealed. The XRD pattern of the resulting alloy composition is shown in FIG. 4.

An anode was prepared and tested as described in Example 1 except that the following components were mixed: 1.90 g of the extruded ribbon, 100 mg SUPER P carbon, and 1.00 g polyimide coating solution. The capacity was 600 mAh/g.

Example 4

An alloy composition $\text{Si}_{41.4}\text{Al}_{39.5}\text{CO}_{13.1}\text{Sn}_2(\text{MM})_4$ was prepared using a procedure similar to that of Example 1 by mixing 28.03 g of aluminum, 30.567 g silicon, 20.408 g cobalt, 6.246 g tin, and 14.748 g mischmetal. The melt-spun sample was annealed by heating at 300° C. for 2 hours under flowing argon. The XRD pattern of the resulting alloy composition is shown in FIG. 5 with the vertical lines indicating the theoretical peak positions for a nanocrystalline $(\text{MM})\text{Sn}_3$ phase.

Example 5

Lithium metal powder was made by chopping 150 micrometer thick lithium foil repeatedly with a razor blade until the maximum dimension of the individual particles were about 150 micrometers. 60 mg of the lithium powder was sprinkled onto a piece cut from the cured electrode described in Example 1 containing 4.62 mg of $\text{Si}_{60}\text{Al}_{14}\text{Fe}_8\text{Ti}_1\text{Sn}_7(\text{MM})_{10}$. The electrode was then placed in-between two pieces of polyethylene film and calendared by means of a hand roller. The resulting electrode was assembled into an electrochemi-

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cal cell versus a lithium counter electrode as described in Example 1. The cell was cycled between 0.9 V vs. metallic Li/Li ion reference electrode and 5 mV vs. metallic Li/Li ion reference electrode at a constant current of 100 mA/g using a cell tester (Maccor Inc., Tulsa Okla.). The voltage versus capacity curve is shown in FIG. 6. The reversible specific capacity was 670 mAh/g.

We claim:

1. A lithium ion battery comprising a cathode, an anode, and an electrolyte in electrical communication with the anode and the cathode, wherein the anode comprises an alloy composition comprising

- a) silicon in an amount of 35 to 70 mole percent;
- b) aluminum in an amount of 1 to 45 mole percent;
- c) a transition metal in an amount of 5 to 25 mole percent;
- d) tin in an amount of 1 to 15 mole percent; and
- e) a fifth element comprising yttrium, a lanthanide element, an actinide element, or a combination thereof in an amount of 2 to 15 mole percent,

wherein each mole percent is based on a total number of moles of all elements except lithium in the alloy composition; and

wherein the alloy composition is a mixture of an amorphous phase comprising silicon and a nanocrystalline phase comprising an intermetallic compound of tin and the fifth element.

2. The lithium ion battery of claim 1, wherein the amorphous phase further comprises aluminum and the transition metal.

3. The lithium ion battery of claim 1, wherein the fifth element comprises cerium, lanthanum, praseodymium, neodymium, or a combination thereof.

4. The lithium ion battery of claim 1, wherein the nanocrystalline phase is substantially free of tin in an elemental form.

5. The lithium ion battery of claim 1, wherein the alloy composition further comprises less than 1 mole percent alkaline earth metal.

6. The lithium ion battery of claim 1, wherein the alloy composition further comprises an alkaline metal.

7. The lithium ion battery of claim 1, wherein the alloy composition comprises particles having a maximum average dimension of 1 to 60 micrometers.

8. The lithium ion battery of claim 1, wherein the alloy composition has a single amorphous phase and a single nanocrystalline phase.

9. The lithium ion battery of claim 1, wherein the alloy composition is of Formula I



wherein

a is a number in the range of 35 to 70;

b is a number in the range of 1 to 45;

T is a transition metal;

c is a number in the range of 5 to 25;

d is a number in the range of 1 to 15;

M is yttrium, a lanthanide element, an actinide element, or a combination thereof;

e is a number in the range of 2 to 15;

the sum of a+b+c+d+e is equal to 100; and

f is a number in the range of 0 to [4.4(a+d)+b].

10. The lithium ion battery of claim 9, wherein the variable a is a number in the range of 40 to 65; b is a number in the range of 1 to 25; c is a number in the range of 5 to 25; d is a number in the range of 1 to 15; and e is a number in the range of 2 to 15.

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11. The lithium ion battery of claim 9, wherein the variable a is a number in the range of 35 to 55; b is a number in the range of 25 to 45; c is a number in the range of 5 to 25; d is a number in the range of 1 to 15; and e is a number in the range of 2 to 15.

12. The lithium ion battery of claim 9, wherein the variable a is a number in the range of 55 to 65; b is a number in the range of 10 to 20; c is a number in the range of 5 to 25; d is a number in the range of 1 to 15; and e is a number in the range of 2 to 15.

13. The lithium ion battery of claim 9, wherein the anode further comprises an organic binder comprising a polyimide.

14. The lithium ion battery of claim 1, wherein the anode further comprises lithium metal.

15. A battery pack comprising at least one lithium ion battery according to claim 1.

16. The lithium ion battery of claim 1, wherein the nanocrystalline phase is substantially free of silicon.

17. A method of preparing a lithium ion battery, said method comprising:

providing an alloy composition comprising

- a) silicon in an amount of 35 to 70 mole percent;
- b) aluminum in an amount of 1 to 45 mole percent;
- c) a transition metal in an amount of 5 to 25 mole percent;
- d) tin in an amount of 1 to 15 mole percent; and
- e) yttrium, a lanthanide element, an actinide element, or a combination thereof in an amount of 2 to 15 mole percent,

wherein each mole percent is based on a total number of moles of all elements except lithium in the alloy composition and wherein the alloy composition is a mixture of an amorphous phase comprising silicon and a nanocrystalline phase comprising an intermetallic compound of tin and the fifth element;

providing a cathode and an electrolyte, wherein the electrolyte is in electrical communication with both the cathode and the anode.

18. The method of claim 17, wherein providing the alloy composition comprises melt spinning the silicon, aluminum, tin, transition metal element, and fifth element.

19. The method of claim 17, wherein providing the alloy composition comprises initially forming a totally amorphous precursor material and then annealing the precursor material to prepare the mixture of the amorphous phase and the nanocrystalline phase.

20. The method of claim 17, wherein providing the alloy comprises

forming a precursor material that comprises

- i) amorphous material;
- ii) the nanocrystalline phase comprising tin and the fifth element; and
- iii) crystalline elemental tin; and

annealing the precursor material to remove the crystalline elemental tin.

21. The method of claim 17, wherein the nanocrystalline phase is substantially free of silicon.

22. An alloy composition comprising

- a) silicon in an amount of 35 to 70 mole percent;
- b) aluminum in an amount of 1 to 45 mole percent;
- c) a transition metal in an amount of 5 to 25 mole percent;
- d) tin in an amount of 1 to 15 mole percent; and

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e) a fifth element comprising yttrium, a lanthanide element, an actinide element, or a combination thereof in an amount of 2 to 15 mole percent,

wherein each mole percent is based on a total number of moles of all elements except lithium in the alloy composition; and

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wherein the alloy composition is a mixture of an amorphous phase comprising silicon and a nanocrystalline intermetallic compound of tin and the fifth element.

23. The alloy composition of claim **22**, wherein the nanocrystalline phase is substantially free of silicon.

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