

ELECTRODE COMPOSITIONS HAVING IMPROVED CYCLING BEHAVIOR

STATEMENT OF PRIORITY

5 This application derives priority from a provisional application filed on January 13, 2000 bearing serial number 60/175,893.

TECHNICAL FIELD

 This invention relates to electrode materials useful in secondary lithium batteries.

BACKGROUND OF THE INVENTION

10 Two classes of materials have been proposed as anodes for secondary lithium batteries. One class includes materials such as graphite and other forms of carbon, which are capable of intercalating lithium. While the intercalation anodes generally exhibit good cycle life and coulombic efficiency, their capacity is
15 relatively low.

 A second class includes metals that alloy with lithium metal. Although these alloy-type anodes generally exhibit higher capacities relative to intercalation-type anodes, they suffer from relatively poor cycle life and coulombic efficiency. One reason is that the alloy-type anodes undergo large volume changes during
20 charge and discharge. This results in the deterioration of contact between the active particles and conductive diluent (e.g., carbon) particles typically combined with the active particles to form the anode. The deterioration of contact, in turn, results in diminished cycling rate behavior.

SUMMARY OF THE INVENTION

25 The invention provides electrode compositions suitable for use in secondary lithium batteries in which the electrode compositions have high initial capacities that are retained even after repeated cycling. The electrode compositions, and batteries incorporating these compositions, are also readily manufactured.

To achieve these objectives, the invention features an electrode composition that includes a plurality of composite particles admixed with a plurality of electrically conductive diluent particles (e.g., electrically conductive carbon particles). The composition may further include a polymeric binder (e.g., a polyvinylidene fluoride binder) in which the composite particles and diluent particles are dispersed.

The composite particles include an electrochemically active metal particle and an electrically conductive layer partially covering the metal particle. In one aspect, the layer is present in an amount no greater than about 75 wt.% of the composite particle. Preferably, the layer is present in an amount no greater than about 50 wt.% of the composite particle, and may be present in an amount no greater than about 25 wt.% of the composite particle. In a second aspect, the layer is present in an amount no greater than about 75 vol.% of the composite particle, and may be present in an amount no greater than about 50 vol.% or 25 vol.% of the composite particle. The layer improves the efficiency of the electrode by reducing the deterioration of electrical contact between the electrochemically active metal particles and the electrically conductive diluent particles during cycling.

An "electrochemically active metal" is a metal that reacts with lithium under conditions typically encountered during charging and discharging in a lithium battery. In contrast, an "electrochemically inactive elemental metal" is a metal that does not react with lithium under those conditions. In both cases, the term "metal" includes materials such as silicon that are sometimes referred to as "metalloids."

An "electrically conductive layer" is a layer having a bulk electrical conductivity at least in the semi-conducting range, e.g., on the order of about 10^{-6} ohm⁻¹ cm⁻¹ or greater.

The expression "partially covering" means that the layer, when the composite particle is contacted with an electrolyte that includes a lithium electrolyte salt, allows the electrolyte to access the underlying electrochemically active metal particle. In some cases, this involves an arrangement in which the layer is in the form of a discontinuous coating on the particle such that the underlying metal particle material is detectable using x-ray photoelectron

spectroscopy (XPS). In other cases, the layer may be porous to enable the electrolyte to penetrate the layer and access the underlying metal particle. The percent porosity of the layer is determined according to the procedure set forth in the Examples, below. Preferably, the layer has a porosity on the order of about 5 90%.

When incorporated in a lithium battery, the electrode composition preferably exhibits (a) a specific capacity of at least about 100 mAh/ per gram of active metal for 30 full charge-discharge cycles and (b) a coulombic efficiency of at least 99% (preferably at least 99.5%, more preferably at least 99.9%) for 30 full 10 charge-discharge cycles when cycled to realize about 100 mAh/per gram of active metal of the composition. Preferably, this level of performance is realized for 500 cycles, more preferably for 1000 cycles.

In another preferred embodiment, the electrode composition, when incorporated in a lithium battery, exhibits (a) a specific capacity of at least about 15 500 mAh per gram of active metal for 30 full charge-discharge cycles and (b) a coulombic efficiency of at least 99% (preferably at least 99.5%, more preferably at least 99.9%) for 30 full charge-discharge cycles when cycled to realize about 500 mAh per gram of active metal of the composition. Preferably, this level of performance is realized for 200 cycles, more preferably for 500 cycles.

20 Examples of suitable metals for the electrochemically active metal particle include aluminum, silicon (e.g., amorphous silicon), tin, antimony, lead, germanium, magnesium, zinc, cadmium, bismuth, and indium. The particle may also include one or more electrochemically inactive elemental metals. Examples of suitable electrochemically inactive elemental metals include Group IB through 25 Group VIIB elemental metals, as well as group VIII and rare earth elemental metals. Specific examples include Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Y, Zr, Nb, Mo, La, Hf, Ta, W, Ce, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu, Be, and Sm. Of this group, molybdenum, niobium, tungsten, tantalum, iron, nickel, manganese, and copper are preferred.

30 In one embodiment, the metal particle consists essentially of at least one electrochemically inactive elemental metal and at least one electrochemically active elemental metal in the form of an amorphous mixture at ambient

temperature. For example, the mixture may consist essentially of silicon, tin, and copper. The mixture remains amorphous when the electrode composition is incorporated into a lithium battery and is cycled through at least one full charge-discharge cycle at ambient temperature. An "amorphous" material is a material
5 that lacks the long range atomic order characteristic of crystalline material, as observed by x-ray diffraction, transmission electron microscopy or differential scanning calorimetry.

The electrically conductive layer may take a number of forms. In one embodiment, the layer includes electrically conductive carbon particles dispersed
10 in a polymeric binder (e.g., a polyvinylidene fluoride binder). In other embodiments, the layer is a metal layer such as a copper or chromium layer. In a particularly preferred embodiment, the composite particles feature a layer of electrically conductive carbon particles dispersed in a polyvinylidene binder partially covering the active metal particle, and the electrode composition is
15 prepared by combining the composite particles with electrically conductive carbon diluent particles in a second polyvinylidene fluoride binder.

Lithium batteries including the above-described electrode compositions may be used as power supplies in a variety of applications. Examples include power supplies for motor vehicles, computers, power tools, and
20 telecommunications devices.

Other features and advantages of the invention will be apparent from the following description of the preferred embodiments thereof, and from the claims.

DESCRIPTION OF DRAWINGS

FIG. 1A illustrates the cycling performance, in terms of reversible specific
25 capacity, of electrodes with and without electrically conductive layers, as described in Example 1.

FIG. 1B illustrates the cycling performance, in terms of coulombic efficiency, of electrodes with and without electrically conductive layers, as described in Example 1.

30 FIG. 2 is an x-ray diffraction profile for the silicon-tin-copper sample having an electrically conductive layer described in Example 2, obtained prior to cycling.

FIG. 3 illustrates the cycling performance of the silicon-tin-copper sample and the silicon-tin-copper sample having an electrically conductive layer described in Example 2 in terms of charge rest voltage and trickle capacity.

FIG. 4 is an x-ray diffraction profile for the silicon sample having an electrically conductive layer described in Example 3, obtained prior to cycling.

FIG. 5 illustrates the cycling performance of the silicon sample and the silicon sample having an electrically conductive layer described in Example 3 in terms of charge rest voltage and trickle capacity.

FIG. 6 is an x-ray diffraction profile for the silicon sample having an electrically conductive layer described in Example 4, obtained prior to cycling.

FIG. 7 illustrates the cycling performance of the silicon sample and the silicon sample having an electrically conductive layer described in Example 4 in terms of charge rest voltage and trickle capacity.

FIG. 8 is an x-ray diffraction profile for the silicon sample having an electrically conductive layer described in Example 5, obtained prior to cycling.

FIG. 9 illustrates the cycling performance of the silicon sample and the silicon sample having an electrically conductive layer described in Example 5 in terms of charge rest voltage and trickle capacity.

FIG. 10 is a series of optical micrographs comparing pre- and post-cycling behavior of samples prepared with and without an electrically conductive layer.

DETAILED DESCRIPTION

The electrode compositions include composite particles admixed with an electrically conductive diluent such as carbon black. The composition may further include a polymeric binder such as polyvinylidene fluoride in which the composite particles and diluent particles are dispersed. The composite particles have the chemical composition and microstructure described in the Summary of the Invention, above. They may be prepared in the form of thin films using techniques such as chemical and vapor deposition, vacuum deposition (i.e., sputtering), vacuum evaporation, melt spinning, splat cooling, spray atomization, electrochemical deposition and the like, and then pulverized. They may also be

prepared using techniques such as ball milling or chemical reduction of the active metal.

The electrode compositions are particularly useful in lithium ion batteries. To prepare a battery, the composite particles and electrically conductive diluent are combined with a binder (e.g., a polyvinylidene fluoride binder) and solvent to form a slurry which is then coated onto a backing using conventional coating techniques and dried to form the electrode. The electrode is then combined with an electrolyte and a counterelectrode.

The electrolyte may be a solid or liquid electrolyte. Examples of solid electrolytes include polymeric electrolytes such as polyethylene oxide, polytetrafluoroethylene, fluorine-containing copolymers, and combinations thereof. Examples of liquid electrolytes include ethylene carbonate, diethyl carbonate, propylene carbonate, and combinations thereof. The electrolyte is provided with a lithium electrolyte salt. Examples of suitable salts include LiPF_6 , LiBF_4 , and LiClO_4 .

Examples of suitable counterelectrode compositions for liquid electrolyte-containing batteries include LiCoO_2 , $\text{LiCo}_{0.2}\text{Ni}_{0.8}\text{O}_2$, and LiMn_2O_4 . Examples of suitable counterelectrode compositions for solid electrolyte-containing batteries include LiV_3O_8 and LiV_2O_5 .

The invention will now be described further by way of the following examples.

EXAMPLES

A. Electrode Preparation

Electrodes were prepared in the form of thin films either by sputtering according to the following procedures.

Sputtering Procedure #1

Thin films were prepared by sequential or single target sputtering using a modified Perkin-Elmer Randex Model 2400-8SA Sputtering System. The original 8 inch diameter of sputter sources were replaced with 6 inch diameter dc magnetron sputtering sources commercially available from Materials Science of

San Diego CA. The sputtering sources were powered using Advanced Energy Model MDX-10 dc sputtering power supplies operating in constant current mode. The turntable drive unit of the Randex System was replaced with a stepper motor to improve rotation speed range and control. The System was pumped with an
5 untrapped oil diffusion pump backed by a conventional rotary vane pump.

Sputtering was performed at argon pressures in the range of 3-30 mTorr. The pressure was maintained by controlling the argon flow in combination with a venetian blind-style conductance limiter placed over the diffusion pump.

A copper foil (thickness = 0.001 inch) was bonded to the water-cooled
10 substrate turntable of the Randex System using double sided adhesive tape (3M Brand Y9415, commercially available from 3M Company of St. Paul, MN). The system was closed and pumped down, typically to base pressures below 1×10^{-5} Torr (the base pressure prior to deposition is not critical). The samples were etched prior to deposition using the "Sputter Etch" mode of the Randex System
15 with 13.56 MHz power applied to the substrate turntable and an argon pressure of 8 mTorr in the sputtering chamber. This procedure caused the copper foil surface to be bombarded with moderate energy argon ions (100-150 eV) to further clean the copper and insure good adhesion of the sputtered film to the copper surface. A typical cleaning cycle was 150W for 30 minutes, with the substrate table rotating
20 during the cycle.

Following etching, the sputtering sources were started up using a mechanical shutter between the sources and the copper substrate. This removed contaminants from the source surface without depositing them on the substrate surface. Next, both sources were started up at pre-determined current levels and
25 deposition initiated. After a suitable deposition time, one or both sources were turned off.

Sputtering Procedure #2

Films were prepared using a sputtering coater consisting of a conventional
30 web handling system driving a 6 inch wide web over a water-cooled chill roll opposing three 6 inch long water-cooled sputtering targets. A multitude of water-cooled shields confined the sputtering plasma and defined the exposed area of the

moving web. The coater was evacuated using a CTI-CRYOGENICS ON-BORD® high vacuum cryo pump and a Leybold high vacuum turbo pump model 220 backed by a conventional roughing pump. The targets were powered by an ADVANCED ENERGY MDX II dc power supply operated in constant power mode. Sputtering was performed at 30mTorr in an argon atmosphere. Adjusting the sputtering power and the web speed controlled the amount of deposited material (coating weight).

Sputtering Procedure #3

Thin films were prepared using individual sputtering targets in a P4 Mill Lane Sputtering System. The sputtering sources were powered using Advanced Energy Model MDX-10 dc sputtering power supplies operating in constant power mode. The system was pumped using six CTI-CRYOGENICS ON-BORD® high vacuum cryo pumps (one 10 in. pump and five 8 in. pumps). A copper foil (thickness = 0.001 inch) was taped to the 24 inch chilled roll of the sputtering system. The system was closed and pumped down, typically to base pressures below 3×10^{-6} Torr. Next, both sources were started up with a 2 minute power ramp to the final power level and deposition initiated. After a suitable deposition time, the silicon was turned off, and a copper or chromium target was turned on to create a top coat.

B. X-Ray Diffraction

Diffraction patterns were collected using a Siemens Model Kristalloflex 805 D500 diffractometer equipped with a molybdenum target x-ray tube and a diffracted beam monochromator. Samples were mounted on the sample holder.

C. Porosity

Porosity is defined in the following equations:

$$P = \frac{V_{pores}}{V_{obs}} = \frac{V_{obs} - V_{ideal}}{V_{obs}} = \frac{\frac{m_{obs}}{\rho_{obs}} - \frac{m_{ideal}}{\rho_{ideal}}}{\frac{m_{observed}}{\rho_{observed}}} = \frac{\rho_{obs}^{-1} - \rho_{ideal}^{-1}}{\rho_{obs}^{-1}}$$

where P is the calculated porosity, V refers to the volume, the subscripts for V indicate which volume is referred to among the volume of the pores, the observed volume, obs, and the ideal volume. Volume may be calculated by dividing the mass m of a given component i by its density ρ . The masses of interest, obs and ideal, are equivalent; thus the porosity can be calculated from the observed and ideal densities alone. The ideal and observed densities are arrived at two different ways. The ideal is calculated as follows:

$$\rho_{ideal} = m_T / V_T = m_T / \left[\sum_i \frac{m_i}{\rho_i} = \left[\sum_i \frac{w_i}{\rho_i} \right]^{-1} \right]$$

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where T refers to the ideal, total, non-porous layer containing i parts, and w_i refers to the weight percent of the total layer due to a given part i. The weight percent of each part of the layer is known when the layer is produced. The density of each part is that supplied by the manufacturer or determined experimentally, and assumes zero porosity of the ideal part. The observed density is calculated as follows:

15

$$\rho_{obs} = m_{Tobs} / V_{Tobs} = m_{Tobs} / [A_{Tobs} t_{Tobs}]$$

where t_{obs} refers to the observed values for the total porous layer, A refers to the area, and t refers to the thickness. The masses of a set of large area layers are averaged. The thickness is an average of a set measured with a micrometer.

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We now describe the preparation and characterization of specific electrode samples.

Example 1

A single target of aluminum-silicon (64 wt.% aluminum and 36 wt.% silicon) was sputtered onto a cleaned, cooled, 1 mil, fully annealed, cold rolled 110 copper backing (Allfoils, Brooklyn Hts., Ohio). Sputtering was accomplished following Sputtering Procedure #1 under 12 mTorr of argon using a substrate rotation rate of 38 rpm and a rate of 24 angstroms/kWmin. The power was 8 kW and the total sputtering time was 4 hours. The sputter-deposited film had a thickness of 4.5 microns and exhibited poor adhesion to the copper substrate.

Next, a layer of copper having a thickness of 1.2 microns was sputter-deposited onto half of the sputter-deposited aluminum-silicon film. Sputtering was accomplished under 12 mTorr of argon using a substrate rotation rate of 38 rpm and a rate of 200 angstroms/kWmin. The power was 2 kW and the total sputtering time was 0.5 hours. Aluminum-silicon films with and without the copper overlayer were then separately peeled off the thick copper backing and converted into flake by pulverizing each film using a mortar and pestle.

A 10% solids dispersion was prepared by combining 2.4 g of each pulverized film with 0.26 g of polyvinylidene fluoride binder and 0.14 g of Super S conductive carbon in N-methyl-2-pyrrolidinone. Each dispersion was then milled with ceramic media in a roller mill overnight at 100 rpm, followed by coating onto a copper foil and drying under vacuum for several hours to remove residual solvent. The resulting coated samples were then used to construct 1225 coin cells using a lithium foil (about 300 micrometers thick, available from Aldrich Chemical Co. of Milwaukee, WI) as the counterelectrode. The cell was constructed using a 50 micrometer thick polyethylene separator. The electrolyte was 1 molar LiPF_6 in a 1:1 v/v mixture of ethylene carbonate and diethyl carbonate. Copper spacers were used as current collectors and to fill void areas in the cell.

The electrochemical performance of the cell was measured using a MACCOR cyler. Cycling was done by constant current charge and discharge between 1.0 V and 0.0 V. The reversible specific capacity and coulombic efficiency of the cell are shown in Figs. 1A and 1B, respectively. The results demonstrate that the electrodes having an electrically conductive copper layer partially covering the active aluminum-silicon particle exhibit superior coulombic

efficiency and cycling performance relative to electrodes featuring aluminum-silicon particles that lack such a layer.

Example 2

5 A film containing 30 wt.% silicon, 66 wt.% tin, and 4 wt.% copper was prepared by sputter deposition according to Sputtering Procedure #2 described above using 11 kW total power for the three individual targets. The sputtering was conducted under 30 mTorr of argon using a web speed of 0.24 ft/min. Three targets of identical silicon/tin/copper composition were sputter deposited at a rate
10 of about 3 grams/kwh. A 10 micron thick copper foil (Japan) was used as the backing. The sputter deposited film had a thickness of about 5 microns and a density of about 4 g/cm³. The film was scraped from the copper foil using a razor blade, pulverized, and sieved using a 270-mesh sieve (U.S. standard sieve size; ASTM E-11-61).

15 The resulting powder was used to construct a 2325 coin cell for cycling experiments. A dispersion was prepared having 50 wt.% of the powder, 32 wt.% Super-P carbon (MMM Carbon, Belgium), and 18 wt.% polyvinylidene fluoride binder in N-methyl-2-pyrrolidinone. The dispersion was then coated onto a second copper foil and dried under vacuum for several hours to remove residual solvent.
20 The resulting coated foil was used to construct the 2325 coin cell using a lithium foil (about 300 micrometers thick, available from Aldrich Chemical Co. of Milwaukee, WI) as the counterelectrode. The cell was constructed using a 50 micrometer thick polyethylene separator. The electrolyte was 1 molal LiPF₆ in a 1:1 v/v mixture of ethylene carbonate and diethyl carbonate. Copper spacers were
25 used as current collectors and to fill void areas in the cell.

 The electrochemical performance of the cell, in terms of trickle charge capacity and charge rest voltage, was measured using a MACCOR cycler. The cell was first discharged at a high rate of 350 mA/g to a fixed capacity of 700 mAh/g to lithiate the electrode. The cell was then charged at a rate of 350 mA/g to a voltage
30 of 1.2V to extract lithium from the electrode. Next, the cell was allowed to rest (zero current) for 15 minutes, after which the cell voltage may drop below 1.0V. The potential at the end of this rest period was recorded as the "charge rest

voltage." It provides a measure of the amount of lithium remaining in the electrode. In general, the higher the charge rest voltage and the more stable it is versus cycle number, the more effectively lithium is being removed.

At the end of the rest period, the cell was charged at a low rate ("trickle charge") of 35 mA/g to 1.2V to remove any lithium not removed at the higher rate (350 mA/g). The trickle charge capacity is a measure of the extent of lithium removal and is thus analogous to coulombic efficiency. In general, the more lithium removed during application of the trickle charge, the less effective the electrode is at giving up lithium during the high rate charge. Accordingly, it is desirable to minimize the trickle charge capacity for a given cycle, and to maintain a low trickle charge capacity after repeated cycling. The results for the silicon-tin-copper sample are shown in Fig. 3.

Next, the above-described procedure was repeated except that prior to sputtering, the copper foil was solution coated prior to sputtering with a binder prepared from 40 wt.% Super-P carbon and 60 wt.% polyvinylidene fluoride in N-methyl-2-pyrrolidinone. The binder was coated onto the foil using an 8 mil notch bar, and then dried under vacuum at 60°C for four hours to remove solvent. The dried binder thickness was about 8 microns and the sputtered film thickness was 5 microns. The volume % of the binder layer in the composite, therefore, is 60%. The binder layer had a porosity of 90%, determined according to the procedure described above. The combined binder/sputtered film composite contained 87 wt.% silicon-tin-copper film and 13 wt.% binder.

The x-ray diffraction profile of the sample is set forth in Fig. 2. It is characterized by the absence of crystalline tin and silicon. The large peaks are due to the copper foil current collector.

The composite was removed from the copper backing using acetone, followed by scraping it from the copper foil. The scraped material was pulverized, sieved, combined with a carbon-containing binder layer, and coated onto a second copper foil to form an electrode as described above. The final dried coating contained 50 wt.% active silicon-tin-copper particles, 32 wt.% Super-P carbon, and 18 wt.% polyvinylidene fluoride, where the amounts of Super-P carbon and polyvinylidene fluoride represent the sum total of these materials in both the layer

on the silicon-tin-copper particles and the dispersion used to form the final electrode.

The electrode was used to construct a 2325 coin cell and tested as described above. The cycling results, terms of trickle charge capacity and charge rest voltage, are shown in Fig. 3, alongside the results of the same material prepared without the electrically conductive layer. The sample prepared with the electrically conductive layer exhibited a higher charge rest voltage and lower trickle charge capacity over a number of cycles, demonstrating that partially covering the silicon-tin-copper particle with an electrically conductive layer of carbon dispersed in polyvinylidene fluoride improves the charge efficiency of the electrode.

Example 3

A copper foil was coated with binder as described in Example 2. Next, a film containing 100 wt.% amorphous silicon was sputter deposited on the dried binder following Sputtering Procedure #3. Sputtering was accomplished under 13 mTorr of argon using a substrate rotation rate of 3.8 rpm and a rate of 40.10 angstroms/kWmin. The power was 5.2 kW and the total sputtering time was 3 hours and 48 minutes. The sputter deposited film had a thickness of 4.8 microns. The binder thickness was 8 microns. Accordingly, the amount of binder relative to the total composite (i.e., sputtered film plus binder) was about 25% by weight and about 60% by volume. The composition of the sputtered film was determined by inductively coupled plasma using a Perkin Elmer Optima 3300 DV.

After sputtering, the composite (sputter deposited silicon film plus binder) was removed from the copper foil using acetone, followed by scraping it from the foil. The scraped material was pulverized and sieved to form a powder.

The x-ray diffraction pattern of the powder is shown in Fig. 4. It is characterized by the absence of crystalline silicon.

The powder was combined with a binder and coated onto a second copper foil to form an electrode following the procedure of Example 2. The final dried coating contained 50 wt.% amorphous silicon, 35 wt.% Super-P carbon, and 15 wt.% polyvinylidene fluoride, where the amounts of Super-P carbon and

polyvinylidene fluoride represent the sum total of these materials in both the layer on the silicon-tin-copper particles and the dispersion used to form the final electrode. The electrode was used to construct a 2325 coin cell and tested as described in Example 2 with the exception that the cell was discharged to a fixed capacity of 1400 mAh/g, rather than 700 mAh/g, to lithiate the electrode. The cycling results, terms of trickle charge capacity and charge rest voltage, are shown in Fig. 5.

For the sake of comparison, an electrode was prepared by combining 0.5 grams of amorphous silicon (Iowa Thin Films, Ames, IA) with a binder containing 30 wt.% polyvinylidene fluoride and 70 wt.% Super P carbon in N-methyl-2-pyrrolidinone to form a dispersion. The dispersion was coated on a copper foil backing (0.5 mil) using a 20 mil knife coater, and dried under vacuum for 4 hours. The final dried coating contained 50 wt.% amorphous silicon, 35 wt.% Super P carbon, and 15 wt.% polyvinylidene fluoride. A 2325 coin cell was then assembled and tested following the procedure described above. The results, in terms of trickle charge capacity and charge rest voltage, are shown in Fig. 5. The sample prepared with the electrically conductive layer of carbon dispersed in polyvinylidene fluoride exhibited a higher charge rest voltage and lower trickle charge capacity over a number of cycles, demonstrating that partially covering the amorphous silicon core with the electrically conductive layer improves the charge efficiency of the electrode.

Example 4

A layered film containing 82.0 wt.% amorphous silicon and 18.0 wt.% chromium was prepared by sputter deposition following Sputtering Procedure #3 using a silicon target and a chromium target. The silicon was sputtered under 13 mTorr of argon onto a copper foil using a substrate rotation rate of 3.8 rpm and a rate of 40.10 angstroms/kWmin. The power was 5.5 kW and the total sputtering time was 2 hours. The sputter deposited silicon film had a thickness of 2.65 microns.

The chromium was sputtered onto the silicon film under 3 mTorr of argon using a substrate rotation rate of 3.8 rpm and a rate of 55 angstroms/kWmin. The

power was 5.5 kW and the total sputtering time was 10 minutes. The sputter deposited chromium film had a thickness of 0.3 microns. The amount of chromium, therefore, was 10% by volume of the composite film. The composition of the sputtered composite film was determined by inductively coupled plasma
5 using a Perkin Elmer Optima 3300 DV.

After sputtering, the composite film was removed from the copper foil by scraping it from the foil. The scraped material was pulverized and sieved to form a powder. The x-ray diffraction pattern of the powder is shown in Fig. 6. It is characterized by the absence of crystalline silicon. The sharp peaks are due only to
10 chromium.

The powder was combined with a binder and coated onto a second copper foil to form an electrode following the procedure of Example 2. The final dried coating contained 50 wt.% silicon-chromium, 35 wt.% Super-P carbon, and 15 wt.% polyvinylidene fluoride. The electrode was used to construct a 2325 coin cell
15 and tested as described in Example 2 with the exception that the cell was discharged to a fixed capacity of 1400 mAh/g, rather than 700 mAh/g, to lithiate the electrode. The cycling results, terms of trickle charge capacity and charge rest voltage, are shown in Fig. 7, along with results for the amorphous silicon electrode prepared as described in Example 3 for the sake of comparison. The sample
20 prepared with the chromium layer exhibited a higher charge rest voltage and lower trickle charge capacity over a number of cycles, demonstrating that partially covering the amorphous silicon particles with an electrically conductive layer of chromium improves the charge efficiency of the electrode.

25 Example 5

A layered film containing 75.3 wt.% amorphous silicon and 24.7 wt.% copper was prepared by sputter deposition following Sputtering Procedure #3 using a silicon target and a copper target. The silicon was sputtered under 13 mTorr of argon onto a copper foil using a substrate rotation rate of 3.8 rpm and a
30 rate of 40.10 angstroms/kWmin. The power was 5.5 kW and the total sputtering time was 3 hours and 2 minutes. The sputter deposited silicon film had a thickness of 4 microns.

The copper was sputtered onto the silicon film under 13 mTorr of argon using a substrate rotation rate of 3.8 rpm and a rate of 250 angstroms/kWmin. The power was 2.0 kW and the total sputtering time was 10 minutes. The sputter deposited copper film had a thickness of 5 microns. The amount of copper, therefore, was 56% by volume of the composite film. The composition of the sputtered composite film was determined by inductively coupled plasma using a Perkin Elmer Optima 3300 DV.

After sputtering, the composite film was removed from the copper foil by scraping it from the foil. The scraped material was pulverized and sieved to form a powder. The x-ray diffraction pattern of the powder is shown in Fig. 8. It is characterized by the absence of crystalline silicon.

The powder was combined with a binder and coated onto a second copper foil to form an electrode following the procedure of Example 2. The final dried coating contained 50 wt.% silicon-copper, 35 wt.% Super-P carbon, and 15 wt.% polyvinylidene fluoride. The electrode was used to construct a 2325 coin cell and tested as described in Example 4. The cycling results, terms of trickle charge capacity and charge rest voltage, are shown in Fig. 9, along with results for the amorphous silicon electrode prepared as described in Example 3 for the sake of comparison. The sample prepared with the copper layer exhibited a higher charge rest voltage and lower trickle charge capacity over a number of cycles, demonstrating that partially covering the amorphous silicon particles with an electrically conductive layer of copper improves the charge efficiency of the electrode.

Example 7

Samples were prepared both with and without an electrically conductive layer as described in Example 2. Electrodes based upon these samples were prepared and cycled at 1 mA/cm^2 to a fixed capacity of 700 mAh/g. Optical micrographs were taken of the electrodes both before and after cycling. The results are shown in Fig. 10. The micrographs show that without the electrically conductive layer, the active metal particles push past the polyvinylidene fluoride binder easily, moving almost independently from the binder, with the result that

the post-cycling micrograph looks very different from the pre-cycling micrograph. In the sample with the electrically conductive layer, however, the pre- and post-cycling micrographs are very similar, demonstrating that the particles have moved very little relative to each other because the active metal particles swell and shrink
5 substantially uniformly upon cycling. This behavior, in turn, translates into improved electrode performance.

Other embodiments are within the scope of the following claims.

WHAT IS CLAIMED IS:

1. An electrode composition for use in a lithium ion battery comprising:
 - (a) a plurality of composite particles, each of which comprises (i) an
5 electrochemically active metal particle and (ii) an electrically conductive layer
partially covering said particle,
wherein said layer is present in an amount no greater than about 75 wt.% of
said composite; and
 - (b) a plurality of electrically conductive diluent particles admixed with
10 said composite particles
2. An electrode composition for use in a lithium ion battery comprising:
 - (a) a plurality of composite particles, each of which comprises (i) an
15 electrochemically active metal particle and (ii) an electrically conductive layer
partially covering said particle,
wherein said layer is present in an amount no greater than about 75 vol.%
of said composite; and
 - (b) a plurality of electrically conductive diluent particles admixed with said
20 composite particles.
3. An electrode composition according to claim 1 or 2 wherein said
metal particle comprises a metal selected from the group consisting of aluminum,
silicon, tin, antimony, lead, germanium, magnesium, zinc, cadmium, bismuth, and
indium.
25
4. An electrode composition according to claim 1 or 2 wherein said
layer comprises electrically conductive carbon particles dispersed in a polymeric
binder.
- 30 5. An electrode composition according to claim 4 wherein said
polymeric binder comprises polyvinylidene fluoride.

6. An electrode composition according to claim 1 or 2 wherein said layer comprises a metal.

7. An electrode composition according to claim 1 or 2 wherein said
5 layer is non-graphitic.

8. An electrode composition according to claim 1 or 2 further comprising a polymeric binder in which said composite particles and said diluent particles are dispersed.

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9. An electrode composition according to claim 8 wherein said polymeric binder comprises polyvinylidene fluoride.

10. An electrode composition according to claim 1 or 2 wherein said
15 layer is porous.

11. A lithium ion battery comprising:

(A) a first electrode comprising:

(a) a plurality of composite particles, each of which comprises
20 (i) an electrochemically active metal particle and (ii) an electrically conductive layer partially covering said particle,

wherein said layer is present in an amount no greater than about 75 wt.% of said composite; and

(b) a plurality of electrically conductive diluent particles
25 admixed with said composite particles;

(B) a counterelectrode; and

(C) an electrolyte separating said electrode and said counterelectrode.

12. A lithium ion battery comprising:

30 (A) a first electrode comprising:

(a) a plurality of composite particles, each of which comprises
(i) an electrochemically active metal particle and (ii) an electrically conductive
layer partially covering said particle,

wherein said layer is present in an amount no greater than about 75 vol.%
5 of said composite; and

(b) a plurality of electrically conductive diluent particles
admixed with said composite particles;

(B) a counterelectrode; and

(C) an electrolyte separating said electrode and said counterelectrode.

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