



- (51) International Patent Classification:
H01M 10/052 (2010.01) *H01M 4/131* (2010.01)
H01M 10/054 (2010.01)
- (21) International Application Number:
PCT/US2016/014487
- (22) International Filing Date:
22 January 2016 (22.01.2016)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
62/112,434 5 February 2015 (05.02.2015) US
- (71) Applicant: BOARD OF REGENTS, THE UNIVERSITY OF TEXAS SYSTEM [US/US]; 201 West 7th Street, Austin, Texas 78701 (US).
- (72) Inventors: MANTHIRAM, Arumugam; 8814 Silverarrow Circle, Austin, Texas 78759 (US). ZHAO, Yubao; 3543 Greystone Drive, Apt. 2038, Austin, Texas 78731 (US).
- (74) Agent: LECOINTE, Michelle M.; Baker Botts L.L.P., 98 San Jacinto Blvd., Suite 1500, Austin, Texas 78701 (US).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

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

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

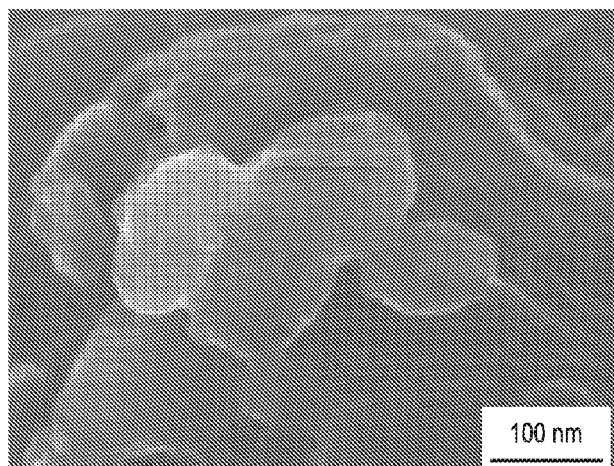
Declarations under Rule 4.17:

- as to the identity of the inventor (Rule 4.17(i))
- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

[Continued on next page]

- (54) Title: BISMUTH-ANTIMONY ANODES FOR LITHIUM OR SODIUM ION BATTERIES

FIG. 3A



(57) Abstract: The present disclosure relates to bismuth (Bi)-antimony (Sb) anodes for use in rechargeable lithium ion (Li⁺) or sodium ion (Na⁺) batteries, to methods of forming electrochemically active Bi-Sb alloys, and to rechargeable batteries containing such anodes.



Published:

— *with international search report (Art. 21(3))*

BISMUTH-ANTIMONY ANODES FOR LITHIUM OR SODIUM ION BATTERIES

TECHNICAL FIELD

5 The present disclosure relates to bismuth (Bi)-antimony (Sb) anodes for use in rechargeable lithium ion (Li^+) or sodium ion (Na^+) batteries, to methods of forming electrochemically active Bi-Sb alloys, and to rechargeable batteries containing such anodes.

BACKGROUND

10 Rechargeable (secondary) lithium ion batteries are widely utilized in consumer electronic devices such as cell phones and laptop computers owing, in part, to their high energy density. Rechargeable lithium ion batteries are also useful in power-intensive applications, such as in electric vehicles and power tools. Additional uses for rechargeable lithium ion batteries, such as in energy grid storage, are possible.

15 Although rechargeable sodium ion batteries are less widespread, they may be used in many of the same applications as lithium ion batteries.

 A rechargeable battery stores electrical energy as chemical energy in two electrodes, an anode and a cathode. The anode and the cathode are electrically insulated from one another inside the battery by an electrolyte and typically also by a
20 separator. The separator is permeable to ions and allows them to pass between the electrodes inside the battery. Electrons (e^-) move through an external electronic circuit. The anode and the cathode normally include compounds into which lithium ions and/or lithium atoms or sodium ions and/or sodium atoms may be reversibly inserted. The electrolyte typically contains a lithium or sodium salt dissolved in an
25 organic liquid to produce lithium ions or sodium ions. Often the electrolyte contains an organic liquid, such as a carbonate, an ether, a nitrile or a sulfoxide.

 When the battery is discharged, electrons move from the anode to the cathode passing through an external device, such as a phone, which is powered by the electron flow, *i.e.* current. The current flowing through the external device can also be of
30 electron vacancies, *i.e.* holes. Lithium ions or sodium ions move from the anode to the cathode at the same time. When the battery is charged, an outside power source, such as a wall socket, supplies the power required for transporting lithium ions or sodium

ions through the electrolyte and electrons through the external circuit from the cathode to the anode. Typically, the lithium or sodium formed from the lithium ions or sodium ions and the electrons, combine with, dissolve in, alloy in, or intercalate in a material of the anode. On discharge the flow of ions and electrons is reversed and
5 the lithium or sodium ions combine with, dissolve in, alloy in, or intercalate in a material of the cathode.

Currently graphite is commonly used as an anode material in lithium ion batteries. Graphite exhibits an operating voltage of very near zero vs. Li/Li^+ , which allows the formation of lithium metal dendrites on the anode. Over time, these
10 dendrites can extend to the cathode and cause the battery to have a short circuit and cease to function. In addition, this low operating voltage allows the formation of a solid-electrolyte interphase (SEI) layer on the electrode surface which passivates the electrode and causes low initial coulombic efficiency and decreased rate capacity, making the battery less desirable to use and/or less long-lived.

Lithium metal suffers from similar problems when used as an anode. Attempts to alleviate these problems by forming lithium metal alloys have only led to new problems, such as steep potential profiles or large volume changes during charging and discharging, which ultimately impairs the structural integrity of the anode and decreases battery life. In addition, many of these alloys operate at near
15 zero vs. Li/Li^+ , allowing the formation of dendrites and/or SEI layers.

Attempts to address some of these problems have included forming particular alloy structures that decrease the effects of volume changes. However, these structures are often complicated and expensive to form. Other attempts include forming alloys that do not experience large volume changes, but these alloys tend to
20 present sloping voltage curves, which causes variations in battery performance and output over the discharge cycle. Such variations are not desirable, as many electrical devices do not tolerate them well or cannot operate with such variations.

Similar problems are exhibited by sodium ion battery anode materials.

BRIEF DESCRIPTION OF THE DRAWINGS

30 The accompanying figures, which are incorporated in and constitute a part of this specification, illustrate several aspects and together with the description serve to explain the principles of the invention.

FIGURE 1 depicts a rechargeable lithium ion battery with an anode containing a Bi-Sb alloy.

FIGURE 2 depicts a high-energy mechanical milling method for forming Bi-Sb alloy.

5 FIGURE 3A is a scanning electron microscopy (SEM) image of the $\text{Bi}_{0.36}\text{Sb}_{0.64}\text{-C}$.

FIGURE 3B is an energy dispersive spectroscopy (EDS) line scan profile along the direction marked in FIGURE 3A.

10 FIGURE 3C is an EDS elemental map of Sb; FIGURE 3D is an EDS elemental map of Bi.

FIGURE 4A is X-ray diffraction (XRD) patterns of the indicated Bi-Sb alloys. The lines in the lower part of the graph are the standard diffraction peaks of Sb (hollow triangle) and Bi (hollow rectangle).

15 FIGURE 4B is the atomic arrangement of a Bi crystal with the lattice pattern shown below the crystal structure.

FIGURE 4C is the atomic arrangement of a $\text{Bi}_{0.57}\text{Sb}_{0.43}$ crystal with the lattice pattern shown below the crystal structure.

FIGURE 4D is the atomic arrangement of a $\text{Bi}_{0.36}\text{Sb}_{0.64}$ crystal with the lattice pattern shown below the crystal structure.

20 FIGURE 4E is the atomic arrangement of a Sb crystals with the lattice pattern shown below the crystal structure.

FIGURES 5A-D present discharge-charge potential profiles of electrodes at galvanostatic condition with a current density of 200 mA g^{-1} . The electrode in FIGURE 5A is Bi-C. The electrode in FIGURE 5B is Sb-C. The electrode in
25 FIGURE 5C is $\text{Bi}_{0.57}\text{Sb}_{0.43}\text{-C}$. The electrode in FIGURE 5D is $\text{Bi}_{0.36}\text{Sb}_{0.64}\text{-C}$.

FIGURES 6A-D present potential profiles of electrodes at the 10th cycle. The electrode in FIGURE 6A is Bi-C. The electrode in FIGURE 6B is Sb-C. The electrode in FIGURE 6C is $\text{Bi}_{0.57}\text{Sb}_{0.43}\text{-C}$. The electrode in FIGURE 6D is $\text{Bi}_{0.36}\text{Sb}_{0.64}\text{-C}$.

30 FIGURE 6E presents capacities of the voltage plateaus of each electrode from FIGURES 6A-D.

FIGURE 7 presents cycle performance of electrodes at galvanostatic condition

with a current density of 200 mA g^{-1} .

FIGURES 8A and B present cycle performance and Coulombic efficiency of electrodes in lithium-ion batteries. The electrode in FIGURE 8A is $\text{Bi}_{0.57}\text{Sb}_{0.43}\text{-C}$. The electrode in FIGURE 8B is $\text{Bi}_{0.36}\text{Sb}_{0.64}\text{-C}$.

5 FIGURES 9A and B present the rate capacities of electrodes. The electrodes in FIGURE 9A are Bi-C and Sb-C. The electrodes in FIGURE 9B are $\text{Bi}_{0.57}\text{Sb}_{0.43}\text{-C}$ and $\text{Bi}_{0.36}\text{Sb}_{0.64}\text{-C}$.

FIGURES 10A-D present potential profiles of the materials in sodium ion batteries. The electrode in FIGURE 10A is Bi-C. The electrode in FIGURE 10B is Sb-C. The electrode in FIGURE 10C is $\text{Bi}_{0.57}\text{Sb}_{0.43}\text{-C}$. The electrode in FIGURE 10D is $\text{Bi}_{0.36}\text{Sb}_{0.64}\text{-C}$.

FIGURE 11A presents cycle performance of electrodes in sodium ion batteries at galvanostatic condition with current at 100 mA g^{-1} .

FIGURE 11B presents C rate performance of electrodes in a sodium ion battery.

FIGURES 12A-D present cyclic voltammetry (CV) scans of the lithiation/delithiation process of electrodes. The electrode in FIGURE 12A is $\text{Bi}_{0.36}\text{Sb}_{0.64}\text{-C}$. The electrode in FIGURE 12B is $\text{Bi}_{0.57}\text{Sb}_{0.43}\text{-C}$. The electrode in FIGURE 12C is Sb-C. The electrode in FIGURE 12D is Bi-C.

20 DETAILED DESCRIPTION

The present disclosure relates to Bi-Sb anodes for use in rechargeable lithium ion or sodium ion batteries, to methods of forming electrochemically active Bi-Sb alloys, and to rechargeable batteries containing such anodes.

The present disclosure relates to an anode 20, which may be included in a rechargeable battery 10. Battery 10 may also include a cathode 30 and an electrolyte 40 as shown in FIGURE 1. Battery 10 may additionally include separator 50. Battery 10 may contain contacts which facilitate connection to an external device 70, which may be powered by the battery or which may recharge the battery. Battery 10 may be a lithium ion or sodium ion battery.

30 Anode 20 includes a Bi-Sb alloy. When lithium ions are present in anode 20, the anode may further contain Li-Bi and/or Li-Sb compounds. The lithiated compounds are typically in the forms of Li_3Bi and Li_3Sb . According to CV studies,

Li₃Sb forms shortly prior to Li₃Bi during discharge. Similarly, when sodium ions are present in anode 20, the anode may further contain Na-Bi and/or Na-Sb compounds, such as Na₃Sb and Na₃Bi. It will be understood by one of skill in the art that the active anode material may contain more or less lithium or sodium depending on the state of charge of anode 20. The ratio of Bi:Sb in anode 20 may range from 1:9 to 9:1. The Bi-Sb alloy may form the same type of crystal regardless of ratios of Bi and Sb. In particular, the Bi-Sb alloy may have a crystal structure in the R-3m space group. The Bi-Sb alloy may be homogenous, as confirmed using XRD.

Carbon, such as elemental carbon (C) may be included in the alloy in order to further enhance conductivity. Carbon may form up to 30% of the alloy by weight, such as up to 20 % by weight. Carbon may be in any form able to enhance conductivity and may be included in the alloy during the alloying process or provided later. Carbon present in the anode may be outside of the Bi-Sb crystals, as may be confirmed using XRD. In particular, it may coat the crystals.

Anode 20 may further include a current collector. In addition, anode 20 may include the Bi-Sb alloy as an active material along with other materials, such as binder or conductivity enhancers.

The operating voltage of anode 20 is approximately 0.8 to 1.0 V vs. Li/Li⁺, with some variation depending on the amount of Bi present. Anode 20 may exhibit a substantially flat voltage plateau. For instance, the voltage may change less than 5% during a time frame that represents 90% of the time required for charge or discharge. Bi and Sb can alloy in any ratio, meaning that formation of Li-Bi and/or Li-Sb compounds or Na-Bi and/or Na-Sb compounds has little effect on the potential of anode 20. The flat voltage plateau allows battery 10 to have a higher energy density, such as 480 Wh/Kg for lithium ion batteries or 330 Wh/Kg for sodium ion batteries.

Furthermore even at high current rates such as 3 A/g, dendrites do not form on anode 20 or do not become sufficiently large to cause the battery to short circuit during normal battery life, such as 300 cycles. This renders battery 10 safer than many other alternatives in which the anode often forms dendrites in at least a substantial number of batteries during normal battery life.

Cathode 30 which may include a cathode material on a current collector. The current collector may be, for example, made of a copper foil or an aluminum foil.

The cathode material may contain a compound that allows reversible insertion of lithium or sodium ions at a potential more oxidizing than that of the anode. The cathode material may also contain an electronic conducting agent or a binder. The cathode material may be selected from transition-metal oxides able to provide a host framework into which lithium ion may be reversibly inserted and extracted. For example, the active cathode material may include a lithium transition-metal oxide, such as LiCoO_2 and $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, a lithium transition-metal polyanion oxide, such as LiFePO_4 or other phosphates, sulfonates, vanadates, or arsenates, oxygen, a peroxide, such as a Li_2O_2 , sulfur, a sulfur-polymers, a sulfoselenides, and any other known or later discovered cathode material for which a compatible electrolyte and suitable voltage may be obtain with an anode as described herein. Also for example, the cathode material may have a layered, olivine, spinel, or rhombohedral NASICON structure.

For sodium ion batteries, suitable cathode materials include $\text{Na}_2\text{FePO}_4\text{F}$, NaVPO_4F , $\text{NaV}_{1-x}\text{Cr}_x\text{PO}_4\text{F}$, Na_xVO_2 , $\text{Na}_4\text{Fe}(\text{CN})_6$, $\text{Na}_{1.5}\text{VPO}_{4.8}\text{F}_{0.7}$, $\text{P2-Na}_x[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$, wherein ($0 < x < 2/3$), sodium-containing layered oxides, and any other known or later discovered cathode material for which a compatible electrolyte and suitable voltage may be obtained with an anode as described herein.

Cathodes and anodes may combine more than one type of electrochemically active material.

The battery may also contain an electrolyte, such as a liquid or a gel in which a lithium salt is dissolved and in which the salt at least partly dissociates to at least one cation and at least one anion. Typically the electrolyte contains an organic liquid having, for example, carbonate, ether, nitrile or sulfoxide functions. In certain embodiments, the lithium salt may be selected from lithium salts conventionally used in lithium ion secondary batteries. Examples of anions of the lithium salt include perfluoroalcanesulfonates, bis(perfluoroalkylsulfonyl) imides, perchlorate (ClO_4^-), hexafluorophosphate (PF_6^-), hexafluoroarsenate (AsF_6^-) or tetrafluoroborate (BF_4^-). The liquid solvent may include an organic liquid, such as a carbonate, particularly an organic carbonate, an ether, a nitrile or sulfoxide, or another ionic liquid. Examples of organic carbonates include propylene carbonate, ethylene carbonate, and dialkyl carbonates (such as cyclic ethylene carbonate, cyclic propylene carbonate, dimethyl-

carbonate, diethylcarbonate and methylpropylcarbonate). The polymer may include a polar polymer selected from solvating, crosslinked or non-crosslinked polymers. A solvating polymer may include a polymer that contains solvating units containing at least one hetero atom chosen from sulfur, oxygen, nitrogen and fluorine. Example
5 solvating polymers include polyethers of linear, comb or block structure, forming or not forming a network, based on poly(ethylene oxide), or polymers containing the ethylene oxide or propylene oxide or allyl glycidyl ether unit, polyphosphazenes, crosslinked networks based on polyethylene glycol crosslinked with isocyanates or networks obtained by polycondensation and bearing groups that allow the
10 incorporation of crosslinkable groups. In another embodiment, the electrolyte may be a solid electrolyte, particularly one with high ionic conductivity such as a graft co-polymer or nanoporous β -Li₃PS₄.

For sodium ion batteries, the equivalents of materials described above for lithium salts, but with sodium in place of lithium, may be used. In particular,
15 propylene carbonate, ethylene carbonate, and dimethylcarbonate, along with a sodium ion or sodium ion source, may be used alone or in combination.

Electrolytes may combine more than one type of electrolyte material.

Batteries of the present disclosure may be as simple as single electrochemical cells. They may also include multiple-cell arrangements, such as multiple cells
20 arranged in series or in parallel. Cell arrangement may be designed to achieve particular parameters for a battery, such as a particular voltage. Batteries may also include regulatory components, such as safety monitors, cut-off switches, fire suppressants, detectors and monitors. In one embodiment, a battery may include a computer.

25 Batteries may be used in a variety of devices, including, but not limited to, cell phones, smart phones, computers, handheld electronic devices, automobiles, including cars, trucks, buses, motorcycles, and powered bicycles, watercraft, including boats and jet-skis, power tools and power tool battery packs, backup power sources, including portable backup power sources, battery-powered medical devices and
30 equipment, and grid storage systems.

There may be a synergistic effect between Bi and Sb in the alloy structure, alleviating the polarization problem common in the Sb lithiation/delithiation process,

significantly improving the initial coulombic efficiency (ICE) of Bi, and enhancing the lithium-ion diffusion rate. Consequently, the Bi-Sb alloy exhibits high ICE, stable cycle performance, and high rate capacity when used in an electrochemical cell or battery.

5 The present disclosure further includes a high-energy mechanical milling method for forming as Bi-Sb alloy such as method 100 depicted in FIGURE 2. In step 110, Bi powder and Sb powder are mixed. The Bi powder and Sb powder may be the same or different average size. Method 110 may result in a more uniform alloy when the powder are the same size. In addition, one or more of the powders may be
10 250 mesh or smaller. However, feedstock size is typically not important because size is adequately reduced in the high-energy mechanical milling process. Other materials may be included as well, such as a carbon source.

 In step 120, the mixed powder is placed in a milling container. For instance, the mixed powder may be placed in a hardened steel chamber. Steps 110 and 120
15 may be combined such that starting materials are mixed in the milling container. Alternatively, starting materials may even be placed in the milling container without mixing prior to the milling process. Milling balls, such as steel milling balls, may also be placed in the milling container. In step 130, the milling container is placed in inert or unreactive atmosphere, such as an argon-filled glovebox. In step 140, the
20 milling container is rotated at a speed of at least 300 rpm or at least 500 rpm for at least 5 hours or at least 12 hours.

 Sb-Bi alloys formed as described above may be used in other applications. For instance, they may form a high-performance thermoelectric material usable at low temperatures, such as 20 - 200K.

25 EXAMPLES

 The present invention may be better understood through reference to the following examples. These examples are included to describe exemplary embodiments only and should not be interpreted to encompass the entire breadth of the invention.

30

Example 1 - Bi-Sb Alloy Formation

 All samples were prepared by a high-energy mechanical milling (HEMM).

Bismuth powder (99.9 %, 100 mesh), antimony powder (99.5 %, 100 mesh), and acetylene black (16.6 wt. %) were mixed and sealed in a hardened steel chamber with steel balls in an argon-filled glovebox. The chamber was then mounted in a PULVERISETTE® (Fritsch GmbH, Germany) 6 planetary mill and rotated at the speed of 500 rpm for 12 h.

Example 2 - SEM-EDS Analysis

SEM-EDS analysis was carried out with a Hitachi S5500 SEM. Two alloy samples with different Bi/Sb molar ratios denoted by $\text{Bi}_{0.57}\text{Sb}_{0.43}\text{-C}$ and $\text{Bi}_{0.36}\text{Sb}_{0.64}\text{-C}$ as well as Bi-C and Sb-C were prepared. FIGURE 3A shows the SEM image of the $\text{Bi}_{0.36}\text{Sb}_{0.64}\text{-C}$ sample, and the elemental distribution of Sb and Bi was characterized by EDS line-scan along the direction marked in the image. As shown in FIGURE 3B, the contents of Bi and Sb keep a constant ratio of around 1.7, which indicates that Bi and Sb are distributed uniformly at the nanometer scale along the line. FIGURES 3C and 3D).

Example 3 - X-Ray Diffraction

XRD data were collected with a Rigaku Ultima-IV X-ray diffractometer with Cu $K\alpha$ radiation and used to confirm the crystal structures of the Bi-Sb alloys as shown in FIGURE 4A. Crystal structures for Bi, Sb, and the two alloys as deduced from XRD are shown in FIGURES 4B-E. Bi and Sb have the same crystal structure (R-3m) and therefore present very similar diffraction patterns with only minor differences in the diffraction angles. The strongest (012) diffraction peaks of Bi and Sb are located, respectively, at 27.2° and 28.6° . For the $\text{Bi}_{0.36}\text{Sb}_{0.64}\text{-C}$ and $\text{Bi}_{0.57}\text{Sb}_{0.43}\text{-C}$ samples, the diffraction patterns are very similar to those of Sb and Bi, and no other new peaks were observed. With the increase in Bi content in the samples, all diffraction peaks shift to lower angles due to the substitution of smaller Sb atoms by larger Bi atoms, strongly indicating the formation of homogeneous Sb-Bi alloy phase.

Lattice parameters are provided in TABLE 1.

TABLE 1 - Lattice Parameters

Samples	Space Group	a (nm) (= b)	c (nm)
Bi	R – 3m	0.4548	1.1866
Sb	R – 3m	0.4303	1.1292
Bi _{0.57} Sb _{0.43}	R – 3m	0.4469	1.1736
Bi _{0.36} Sb _{0.64}	R – 3m	0.4391	1.1409

5 *Example 4 - Electrochemical Cells*

In all test electrochemical cells discussed herein, the electrodes were prepared by doctor-blade coating a slurry onto a copper foil. The slurry contained active material, Super P (conductivity enhancer agent), and Poly(vinylidene fluoride) (PVDF, as binder) with a weight ratio of 70 : 15 : 15. N-Methyl-2-pyrrolidone (NMP)
10 was employed to adjust the viscosity of the slurry. The electrodes had a diameter of 1.2 cm and the active material (metal alloy-carbon composite) loading was *ca.* 2 mg per electrode.

The battery performance of the electrodes was assessed with in CR2032 coin cells with Celgard polypropylene as a separator and Li metal as the counter/reference
15 electrode. The coin cells were assembled in an Argon-filled glovebox. The electrolyte for lithium ion cell was 1 M LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1: 1 v/v). For the sodium ion cell, glass fiber was employed as the separator. The electrolyte was composed of 1 M NaClO₄ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1: 1 v/v) containing 5 (wt.) % fluoroethylene carbonate (FEC) as an
20 additive.

Example 5 - Galvanostatic Measurements

Charge/discharge performance was assessed with an battery cycler under galvanostatic condition in the voltage window of 0.05 - 2 V. As shown in FIGURES 5A and 5B, both Bi-C and Sb-C composite electrodes exhibit flat delithiation potential

plateaus at 0.9 and 1.0 V vs. Li^+/Li , respectively. However, the Bi-C electrode exhibits a large irreversible capacity loss in the first cycle and the ICE was as low as 58 %. Such a low ICE may result from the electrolyte decomposition and formation of SEI on Bi surface, which may eventually waste the limited lithium source in the cathode of a full cell. For the Sb-C electrode, although it has a high ICE of 85 % (TABLE 2), polarization becomes increasingly severe in the first few cycles due to the volume change caused pulverization of Sb particles in the electrode.

However, when the homogeneous Bi-Sb alloy structure is formed, the electrodes show both high ICE and expanded flat plateau. The ICE of the $\text{Bi}_{0.57}\text{Sb}_{0.43}$ -C and $\text{Bi}_{0.36}\text{Sb}_{0.64}$ -C electrodes reach, respectively, as high as 81.7 % and 83.1 %, which will greatly increase the utilization efficiency of the limited lithium source of the cathode in a full cell (FIGURES 5C and 5D and TABLE 2). Taking the delithiation potential profiles of the electrodes at the 10th cycle as examples, the flat-plateau capacities of the Bi-C and Sb-C electrodes are, respectively, 122 and 246 mA h g⁻¹, while those of the $\text{Bi}_{0.57}\text{Sb}_{0.43}$ -C and $\text{Bi}_{0.36}\text{Sb}_{0.64}$ -C electrodes are, respectively, increased to 292 and 360 mA h g⁻¹ (FIGURE 6). The expanded potential flat-plateau of the anode allows maximum energy density of the full cell.

TABLE 2 - Initial Coulombic Efficiencies (ICE) of the electrodes in lithium-ion and sodium-ion batteries.

Samples	ICE (%)	
	LIB ^{a)}	NIB ^{b)}
Bi-C	58.7	66.2
Sb-C	85.8	78.2
$\text{Bi}_{0.57}\text{Sb}_{0.43}$ -C	81.7	78.9
$\text{Bi}_{0.36}\text{Sb}_{0.64}$ -C	83.1	79.6

^{a)} Lithium ion battery; galvanostatic condition with a current density of 200 mA g⁻¹.

^{b)} sodium-ion battery; galvanostatic condition with a current density of 100 mA g⁻¹.

The cycle performance of the electrodes was assessed with galvanostatic conditions at a current density of 200 mA g^{-1} (FIGURE 7). The delithiation capacity of the Sb-C and Bi-C electrodes decays very fast and, only 42 % and 21% of the initial delithiation capacity retain after 50 cycles. The cycle stability is significantly improved when Bi and Sb formed a homogeneous alloy structure. For the $\text{Bi}_{0.36}\text{Sb}_{0.64}$ -C electrode, the initial delithiation capacity is 494 mA h g^{-1} , and at the 100th and 300th cycle, the capacity retention is, respectively, 350 and 249 mA h g^{-1} . The $\text{Bi}_{0.57}\text{Sb}_{0.43}$ -C electrode delivers an initial delithiation capacity of 410 mA h g^{-1} , and 85 % and 72% of the delithiation capacity are retained at the 100th and 300th cycle, corresponding to 0.09% capacity decay per cycle. The coulombic efficiency reaches as high as 99.5% after the first few cycles and remain constant in the subsequent cycles for both the alloy electrodes (FIGURE 8). The tap density of $\text{Bi}_{0.57}\text{Sb}_{0.43}$ -C and $\text{Bi}_{0.36}\text{Sb}_{0.64}$ -C are, respectively, 1.8 and 1.7 g cm^{-3} . The homogeneous alloy matrix of Bi-Sb significantly improved capacity retention.

The rate capacity of the electrodes was also measured at the galvanostatic condition. As shown in FIGURE 9, with the increase of the current density, the specific capacity decays rapidly for both the Sb-C and Bi-C electrodes. At the current density of $2,000 \text{ mA g}^{-1}$, their capacities drop to $< 50 \text{ mA h g}^{-1}$; and there is almost no capacity at the current density of $3,000 \text{ mA g}^{-1}$. This indicates that the lithium-ion diffusion rates in Bi-C and Sb-C electrodes are low. As shown in FIGURE 9B, the delithiation capacity of $\text{Bi}_{0.36}\text{Sb}_{0.64}$ -C is 524, 483, 459, 430, and 396 mA h g^{-1} at the current density of 100 (0.23 C), 500 (1.15 C), 1,000 (2.30 C), 2,000 (4.60 C), and 3000 mA g^{-1} (6.90 C). After the high current cycle performance test, the capacity still reaches as high as 501 mA h g^{-1} at a current density of 100 mA g^{-1} , which is 96 % of the initial delithiation capacity. $\text{Bi}_{0.57}\text{Sb}_{0.43}$ -C also exhibits excellent rate performance (FIGURE 9B). The delithiation capacities at the current density of 100 (0.26 C), 500 (1.30 C), 1,000 (2.60 C), 2,000 (5.20 C), and $3,000 \text{ mA g}^{-1}$ (7.80 C) are, respectively, 441, 431, 385, 355, and 326 mA h g^{-1} . The capacity in the subsequent cycles at the current density of 100 mA g^{-1} reaches 410 mA h g^{-1} , which is 93 % of the initial delithiation capacity. The high C-rate performance of the alloy indicates that the homogeneous Bi-Sb alloy structure is favorable to electron and lithium-ion transport.

The sodium ion battery performance of the electrodes was measured by galvanostatic method with different current densities. As shown in FIGURES 10A and 10B, both the Bi-C and Sb-C electrodes show three potential plateaus at the second sodiation process, which is obviously different from the first cycle. In the phase diagram of Sb-Na, there are two known alloy compounds: NaSb and Na₃Sb. It has been reported that the sodiation/desodiation mechanism is quite different from the lithiation/delithiation process. The formation of an amorphous intermediate phase Na_xSb ($x < 3$) results in the additional plateau (FIGURE 10B). There are also two known Bi-Na alloy compounds: NaBi and Na₃Bi. The sodiation/desodiation process of Bi, also showing three sodiation plateaus, may be similar to that of Sb. The ICE of the Bi-C and Sb-C electrodes are, respectively, 66.2 and 78.2 %. While with the alloy electrodes, the ICE of Bi_{0.57}Sb_{0.43}-C and Bi_{0.36}Sb_{0.64}-C are, respectively, increased to 78.9 and 79.6 % (TABLE 2).

The cycle stability of the electrodes was measured in the half-cell with sodium as the counter/reference electrode at a current density of 100 mA g⁻¹. For the Sb-C and Bi-C electrodes, their respective first desodiation capacity is 384 and 500 mA h g⁻¹. The capacity decays rapidly and the retained capacity of Bi-C electrode is only 173 mA h g⁻¹ at 20th cycle. With the Sb-C electrode, the 20th cycle capacity is as low as 59 mA h g⁻¹ (FIGURE 11A). The fast capacity fade results from severe volume expansion caused by the insertion of the sodium-ion with large radius. As to the alloy electrodes, their cycle performance in sodium ion batteries are more sensitive to the composition of the alloy than that in lithium ion batteries. As shown in FIGURE 11A, the first cycle desodiation capacity of Bi_{0.36}Sb_{0.64}-C electrode is 428 mA h g⁻¹, and it decays to 113 mA h g⁻¹ after 50 cycles. While with Bi_{0.57}Sb_{0.43}-C, the cycle stability largely improves and the 50th cycle desodiation capacity is 293 mA h g⁻¹, corresponding to 0.4 % capacity decay per cycle. In addition, Bi_{0.57}Sb_{0.43}-C exhibits good rate performance. The delithiation capacities at the current density of 100 (0.26 C), 200 (0.52 C), 300 (0.78 C), 500 (1.3 C), and 1,000 mA g⁻¹ (2.6 C) are, respectively, 393, 370, 362, 357, and 326 mA h g⁻¹. After the high C rate cycles, the capacity in the subsequent cycle at a current density of 100 mA g⁻¹ reaches 370 mA h g⁻¹, which is 94 % of the initial desodiation capacity (FIGURE 11B). The Bi-Sb alloy structure may function as a stable host for fast sodiation/desodiation process.

Moreover, the volumetric capacity is more important than gravimetric capacity in certain applications. $\text{Bi}_{0.36}\text{Sb}_{0.64}\text{-C}$ and $\text{Bi}_{0.57}\text{Sb}_{0.43}\text{-C}$ have high tap densities of, respectively, 1.7 and 1.8 g cm^{-3} . The high tap density of the alloy electrodes result in high volumetric capacities in lithium ion batteries and sodium ion batteries.

5 *Example 6- Cyclic Voltammetry Measurements*

Cyclic voltammetry scan was conducted on VoltaLab PGZ402 at a scan rate of 0.05 mV s^{-1} between the voltage window of 0.05 and 2.0 V. FIGURE 12 shows the CV scan profiles of the initial three cycles of the alloy electrodes at a scan rate of 0.05 mV s^{-1} between 0 and 2 V (vs. Li^+/Li). The broad current peak at 0.66 V in the first lithiation scan of $\text{Bi}_{0.36}\text{Sb}_{0.64}\text{-C}$ electrode shifts to higher voltage and split into three current peaks at 0.83, 0.78, and 0.74V (FIGURE 12A). The current peak at 0.83 V corresponds to the transition of Sb to Li_3Sb ; the peaks at 0.78 and 0.74 V are, respectively, attributed to the conversion of Bi to LiBi and Li_3Bi phases. During the anodic scan, the current peaks at 0.93 and 1.06 V result from the delithiation of Li_3Bi and Li_3Sb , producing Bi-Sb alloy. For the $\text{Bi}_{0.36}\text{Sb}_{0.64}\text{-C}$ electrode, the current peaks appear at the same voltage but with different peak intensity due to the difference in the Bi/Sb molar ratio (FIGURE 12B).

As shown in FIGURE 12C, the cathodic and anodic current peaks of Sb-C occur, respectively, at 0.78 and 1.21 V, while in the alloy, the cathodic and anodic current peaks shift, respectively, to higher and lower voltages of 0.83 and 1.06 V. This indicates that the formation of Bi-Sb alloy phase is positive to alleviate the polarization during the lithiation/delithiation of Sb. With the Bi-C electrode, the current peaks of Bi lithiation and delithiation are located at the same voltage to that in the alloy structure (FIGURE 12D). At the first cycle, the anodic current peaks at 1.29 and 1.64 V are derived from the electrolyte decomposition and SEI layer formation on Bi surface, leading to large initial capacity loss. While when Bi atoms are homogeneously dispersed in the Bi-Sb alloy matrix, these peaks disappear, indicating the side reactions on the Bi surface have been effectively restricted.

Although only exemplary embodiments of the invention are specifically described above, it will be appreciated that modifications and variations of these examples are possible without departing from the spirit and intended scope of the invention. For example, throughout the specification particular measurements are

given. It would be understood by one of ordinary skill in the art that in many instances particularly outside of the examples other values similar to, but not exactly the same as the given measurements may be equivalent and may also be encompassed by the present invention. As another example, one of ordinary skill in the art would

5 recognize that, in at least some embodiments, a lithium ion battery or a sodium ion battery may also include batteries where the alkali metal is a mixture of sodium and lithium.

CLAIMS

1. A rechargeable battery comprising:
an anode comprising a bismuth (Bi)-antimony (Sb) alloy;
a cathode; and
5 an electrolyte comprising an ion.
2. The battery of Claim 1, wherein the ratio of Bi:Sb is between 1:9 and 9:1.
- 10 3. The battery of Claim 1, wherein the ion is a lithium ion (Li^+).
4. The battery of Claim 3, wherein the anode further comprises a Li-Bi compound.
- 15 5. The battery of Claim 3, wherein the anode further comprises a Li-Sb compound.
6. The battery of Claim 3, wherein the anode further comprises both a Li-Bi compound and a Li-Sb compound.
- 20 7. The battery of Claim 1, wherein the ion is a sodium ion (Na^+).
8. The battery of Claim 7, wherein the anode further comprises a Na-Bi compound.
- 25 9. The battery of Claim 7, wherein the anode further comprises a Na-Sb compound.
10. The battery of Claim 7, wherein the anode further comprises both a
30 Na-Bi compound and a Na-Sb compound.
11. The battery of Claim 1, wherein the Bi-Sb alloy is homogenous.

12. The battery of Claim 1, wherein the Bi-Sb alloy has a crystal structure in the R-3m space group.

5 13. The battery of Claim 1, wherein the anode further comprises elemental carbon (C).

14. The battery of Claim 1, where the voltage changes less than 5% during a time frame that represents 90% of the time required for charge or discharge of the
10 battery.

15. The battery of Claim 1, wherein the cathode comprises a transition-metal oxide able to provide a host framework into which the ion may be reversibly inserted and extracted.

15

16. The battery of Claim 1, wherein the ion comprises lithium ion and the cathode comprises a lithium transition-metal oxide.

17. The battery of Claim 1, wherein the ion comprises lithium ion and the
20 cathode comprises a lithium transition-metal polyanion oxide.

18. The battery of Claim 1, wherein the ion comprises lithium ion and the cathode comprises a peroxide.

25 19. The battery of Claim 1, wherein the ion comprises lithium ion and the cathode comprises sulfur.

20. The battery of Claim 19, wherein the ion comprises lithium ion and the cathode comprises a sulfur-polymer.

30

21. The battery of Claim 1, wherein the ion comprises lithium ion and the cathode comprises a sulfoselenide.

22. The battery of Claim 1, wherein the ion comprises sodium ion and the cathode comprises $\text{Na}_2\text{FePO}_4\text{F}$.
- 5 23. The battery of Claim 1, wherein the ion comprises sodium ion and the cathode comprises NaVPO_4F .
24. The battery of Claim 1, wherein the ion comprises sodium ion and the cathode comprises $\text{NaV}_{1-x}\text{Cr}_x\text{PO}_4\text{F}$.
- 10 25. The battery of Claim 1, wherein the ion comprises sodium ion and the cathode comprises Na_xVO_2 .
26. The battery of Claim 1, wherein the ion comprises sodium ion and the cathode comprises $\text{Na}_4\text{Fe}(\text{CN})_6$.
- 15 27. The battery of Claim 1, wherein the ion comprises sodium ion and the cathode comprises $\text{Na}_{1.5}\text{VPO}_{4.8}\text{F}_{0.7}$.
- 20 28. The battery of Claim 1, wherein the ion comprises sodium ion and the cathode comprises $\text{P2-Na}_x[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$, wherein $(0 < x < 2/3)$.
29. The battery of Claim 1, wherein the ion comprises sodium ion and the cathode comprises a sodium-containing layered oxide.
- 25 30. The battery of Claim 1, wherein the electrolyte comprises an organic liquid and a salt of the ion.
31. The battery of Claim 1, wherein the battery comprises a regulatory component.
- 30 32. The battery of Claim 1, wherein the battery comprises a computer.

33. A method of forming a bismuth (Bi)-antimony (Sb) alloy comprising:
mixing a Bi powder and a Sb powder, both with a grain size of 250 mesh or smaller;
- 5 placing the powder in a milling box;
placing the milling box in an inert or unreactive atmosphere;
rotating the milling box in the inert or unreactive atmosphere at a speed of at least 300 rpm for at least 5 hours.
- 10 34. The method of Claim 33, further comprising mixing a carbon source with the Bi powder and the Sb powder.
35. The method of Claim 33, wherein rotation comprises rotating the milling box for at least 500 rpm for at least 12 hours.

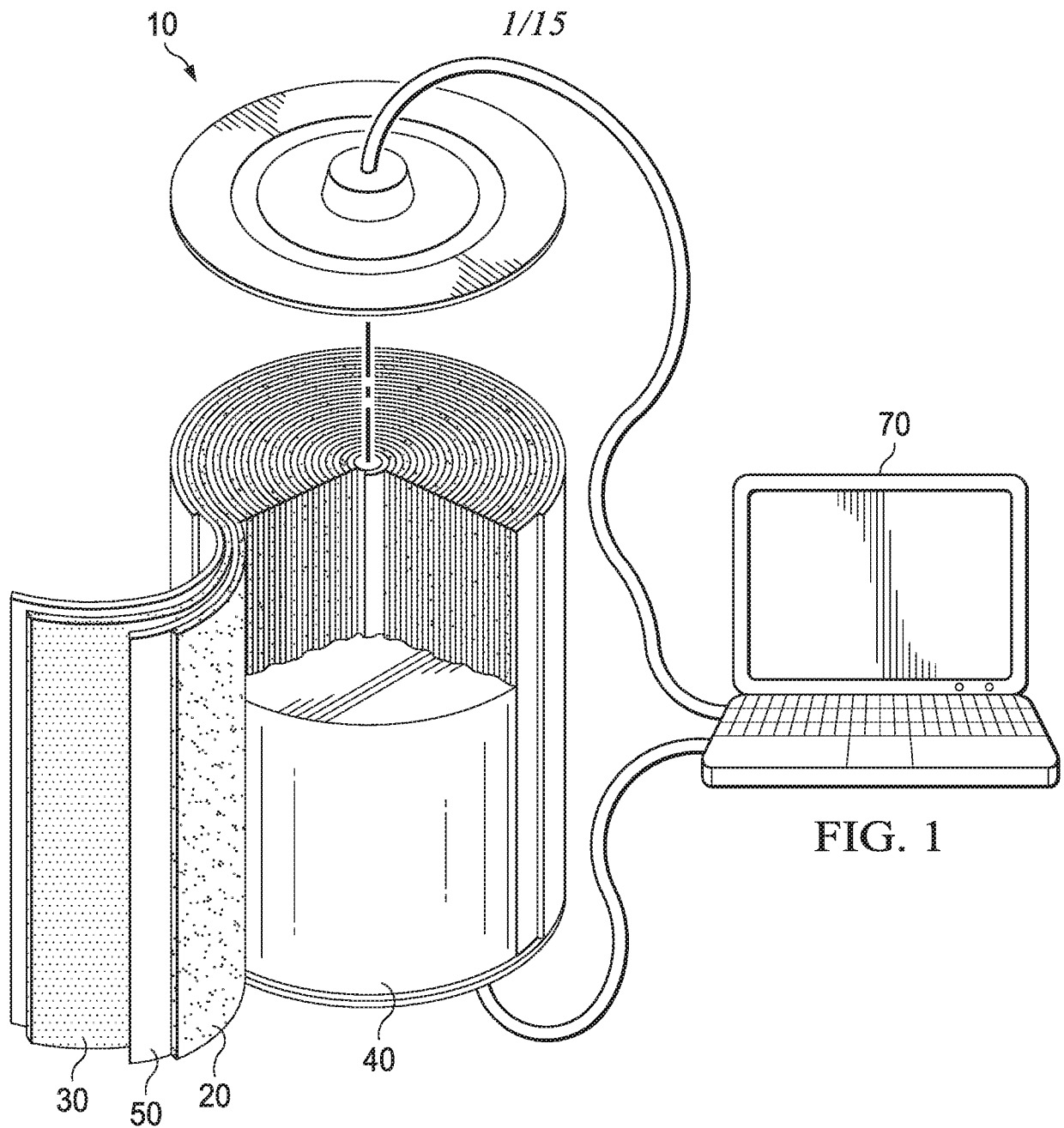


FIG. 1

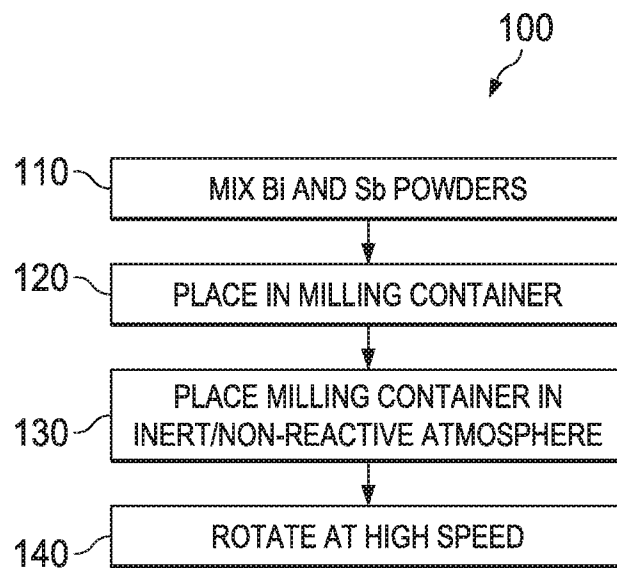


FIG. 2

2/15

FIG. 3A

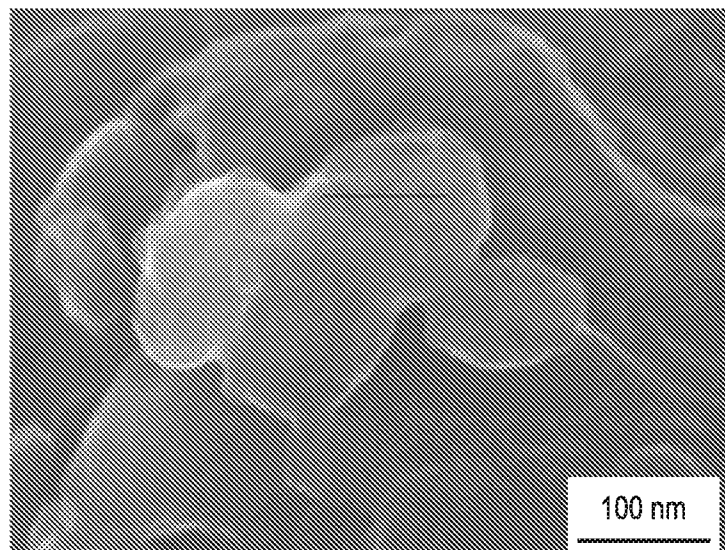
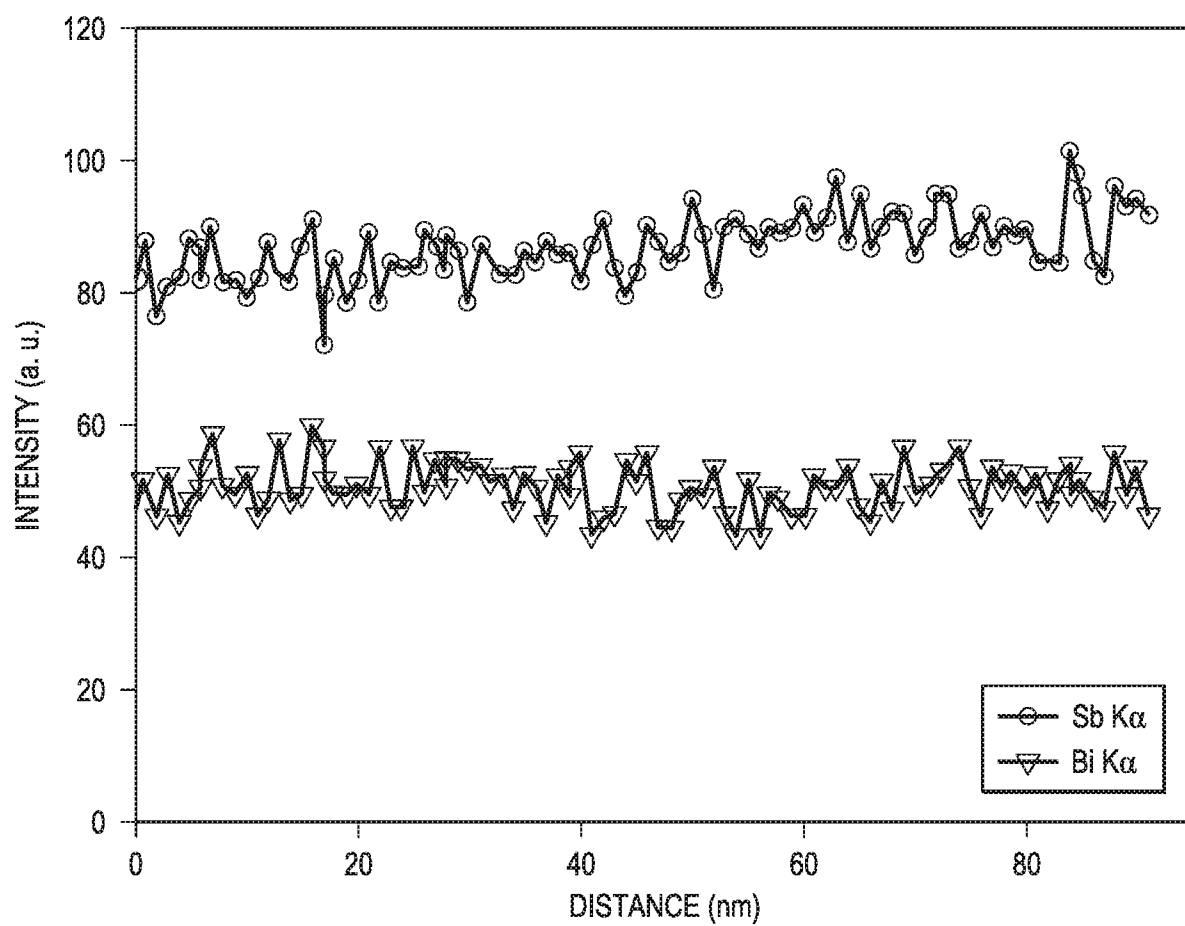


FIG. 3B



3/15

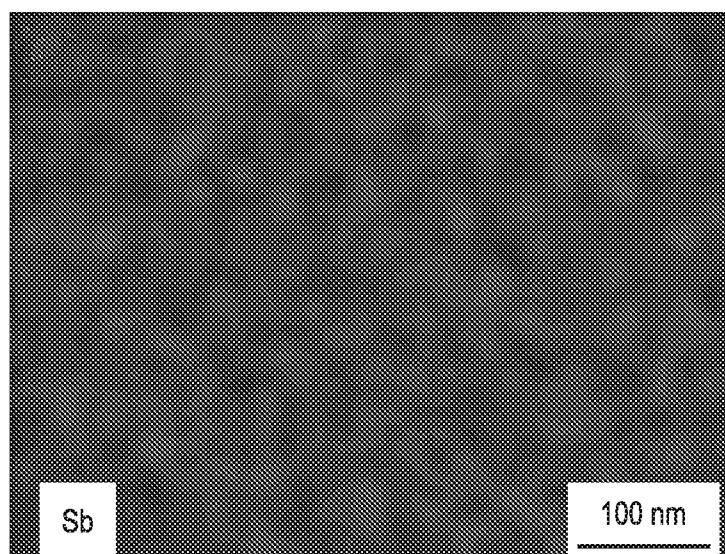


FIG. 3C

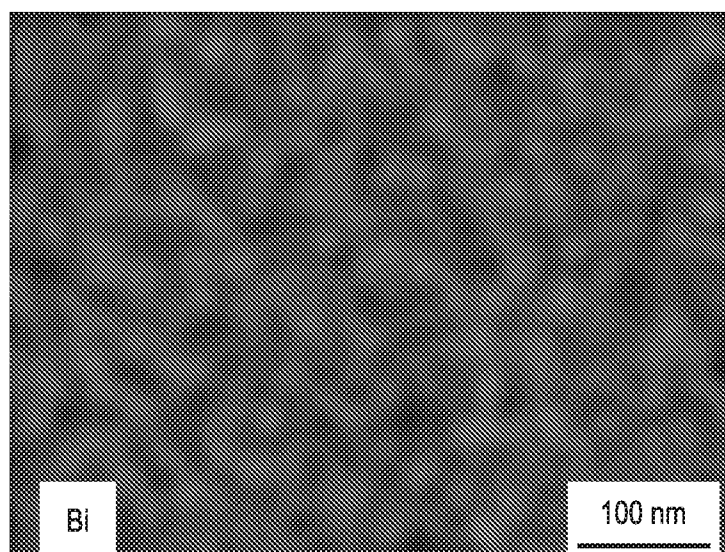
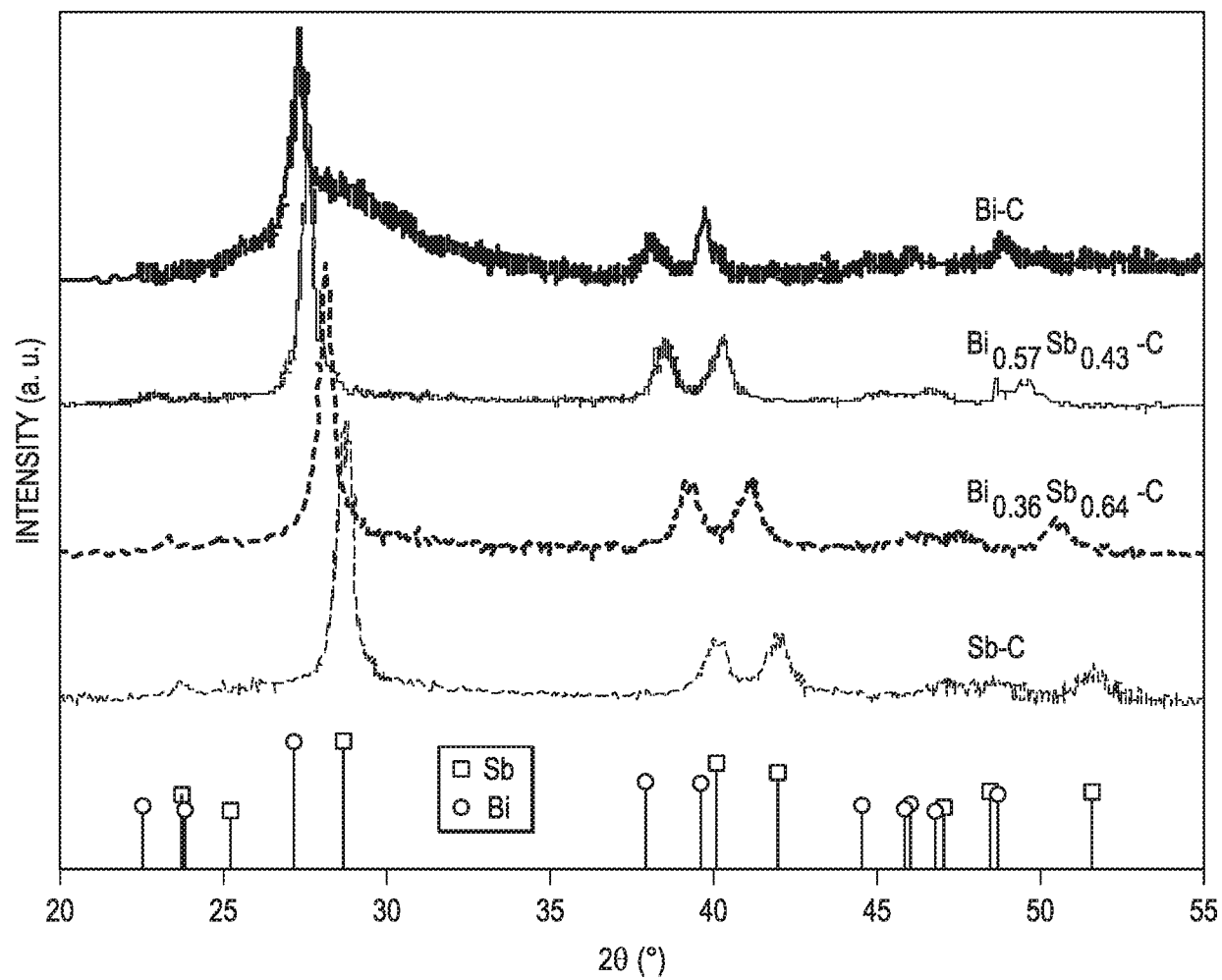
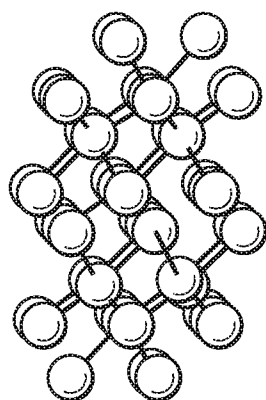


FIG. 3D

4/15

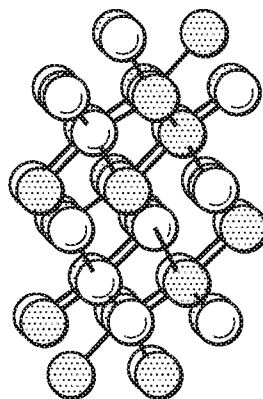
FIG. 4A





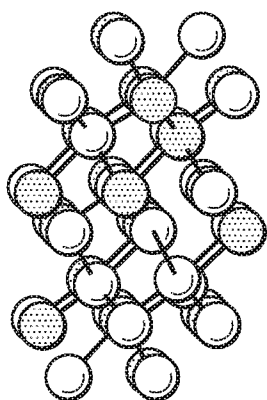
Bi
 $a = 0.4548 \text{ nm}$
 $c = 1.1866 \text{ nm}$

FIG. 4B



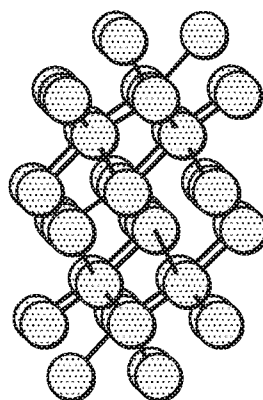
$\text{Bi}_{0.36}\text{Sb}_{0.64}$
 $a = 0.4391 \text{ nm}$
 $c = 1.1409 \text{ nm}$

FIG. 4D



$\text{Bi}_{0.57}\text{Sb}_{0.43}$
 $a = 0.4469 \text{ nm}$
 $c = 1.1736 \text{ nm}$

FIG. 4C



Sb
 $a = 0.4303 \text{ nm}$
 $c = 1.1292 \text{ nm}$

FIG. 4E

6/15

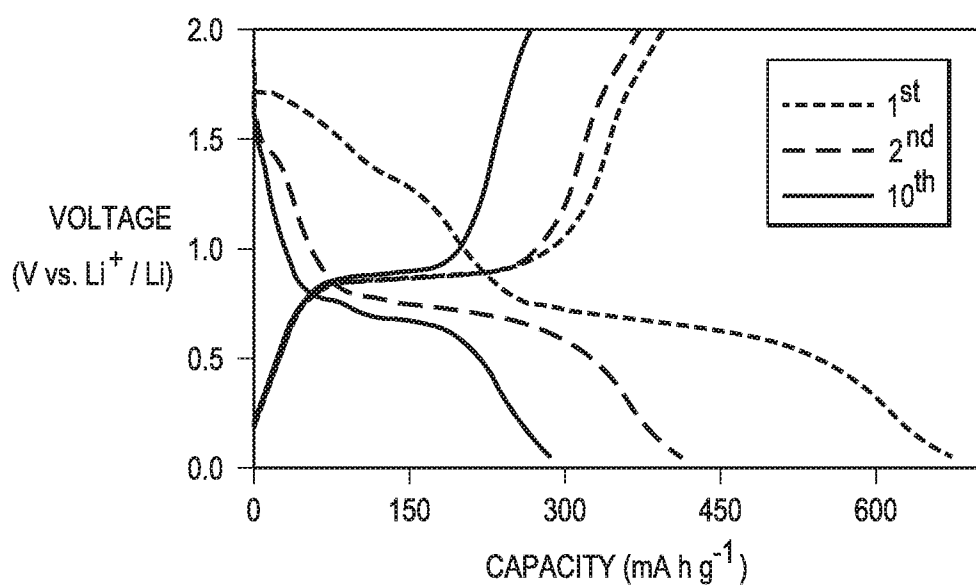


FIG. 5A

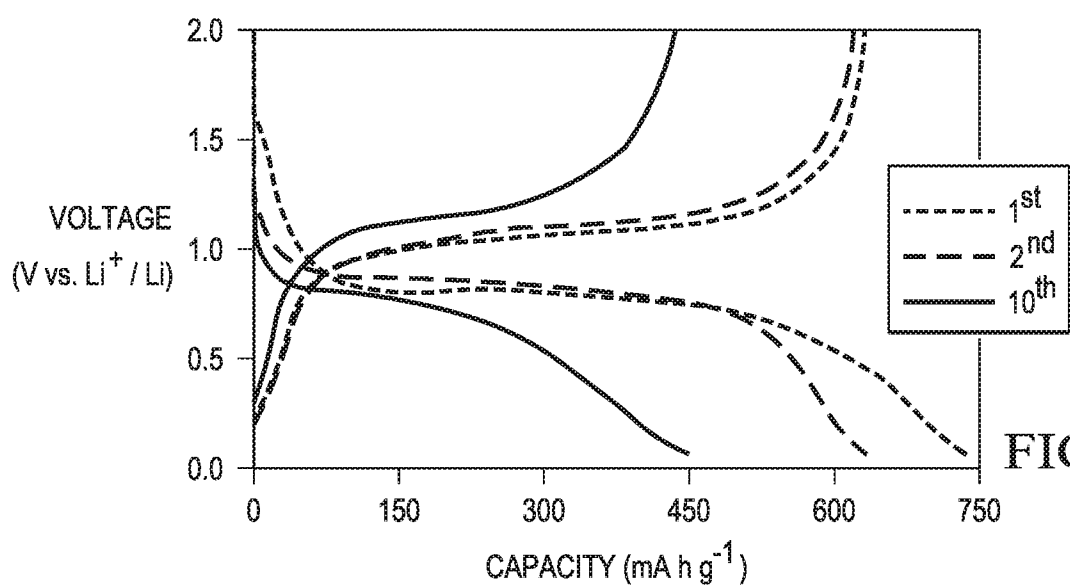


FIG. 5B

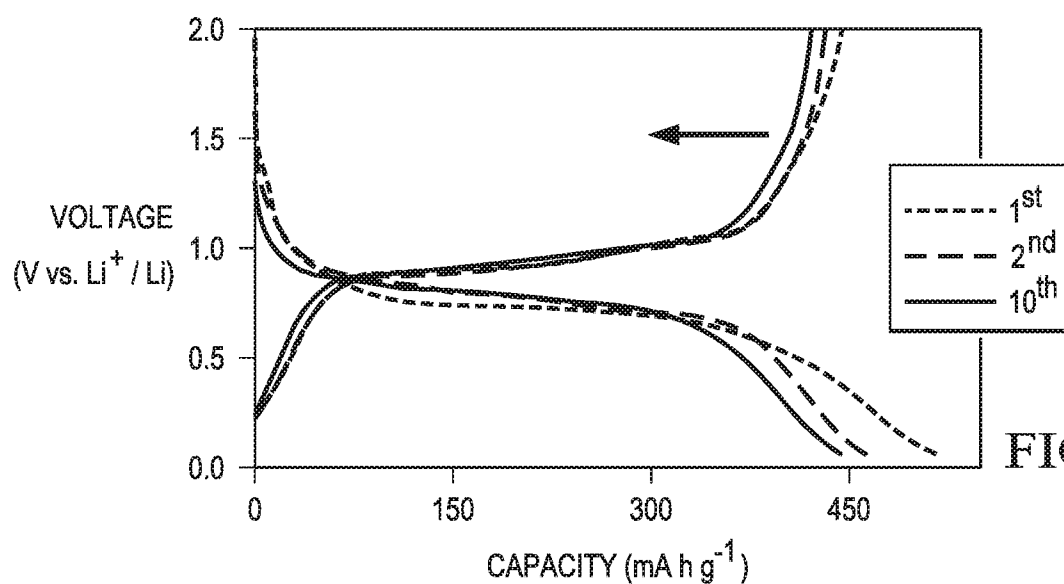
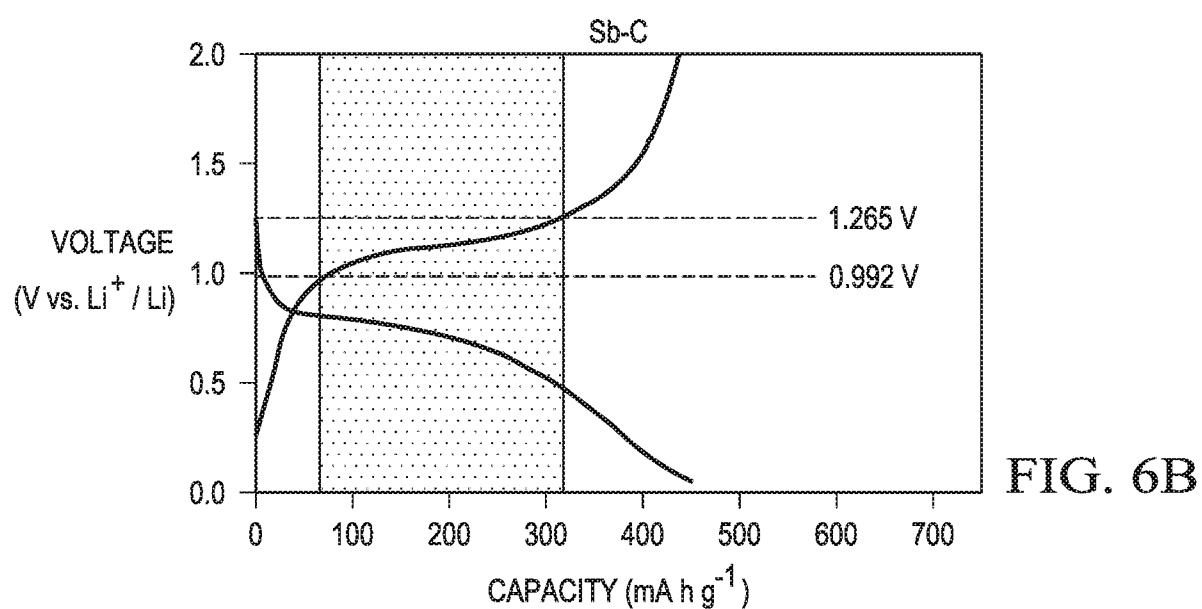
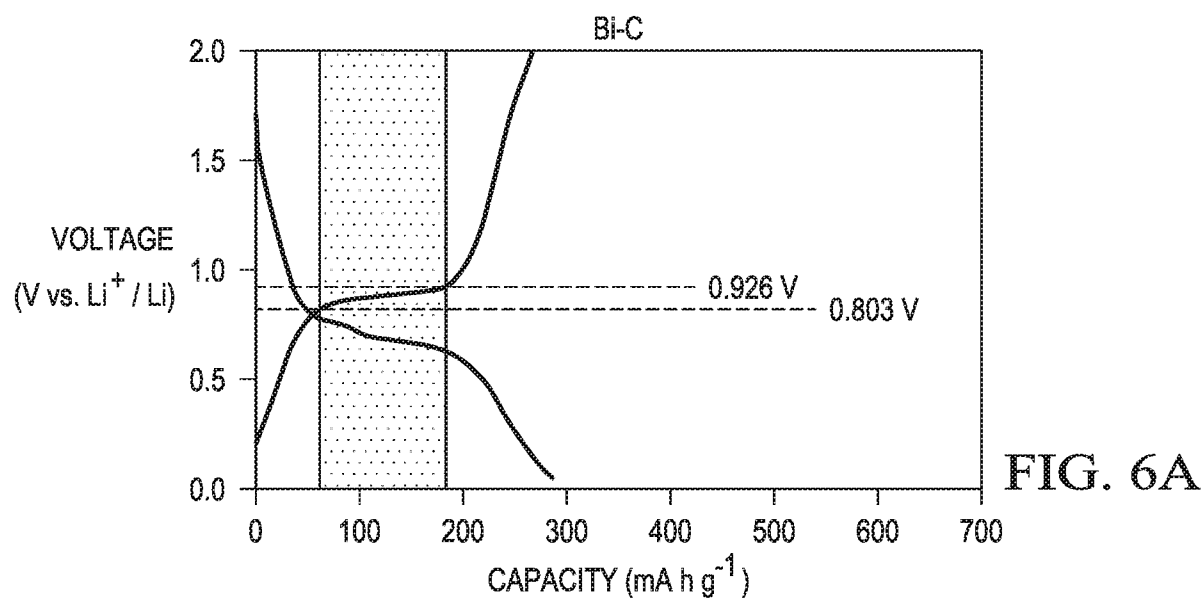
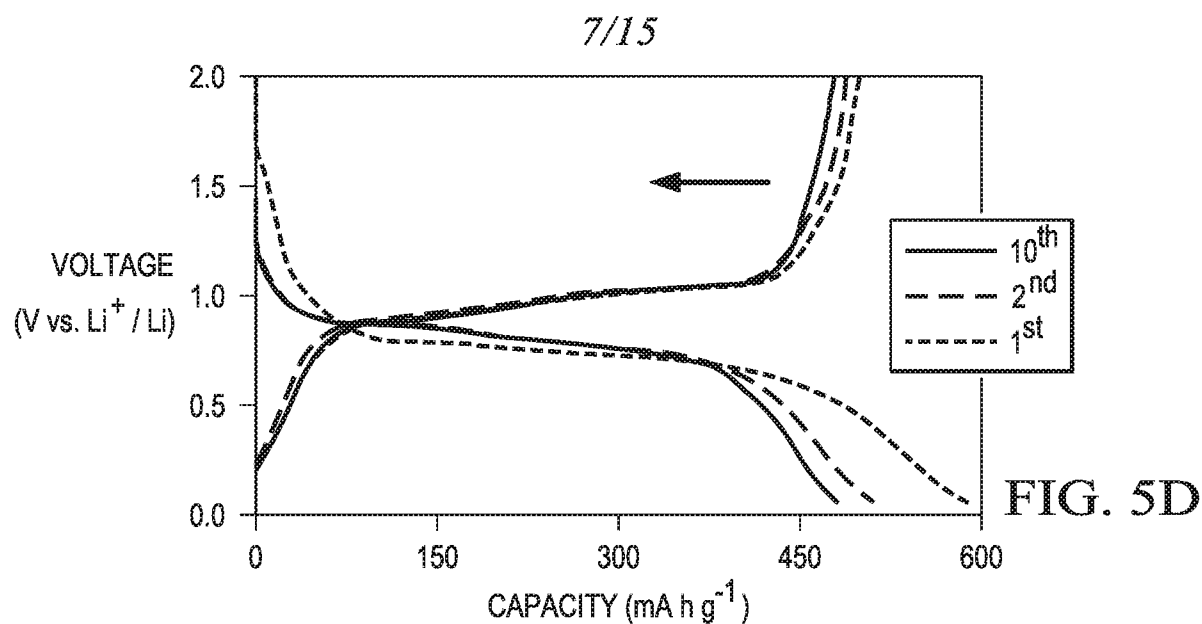
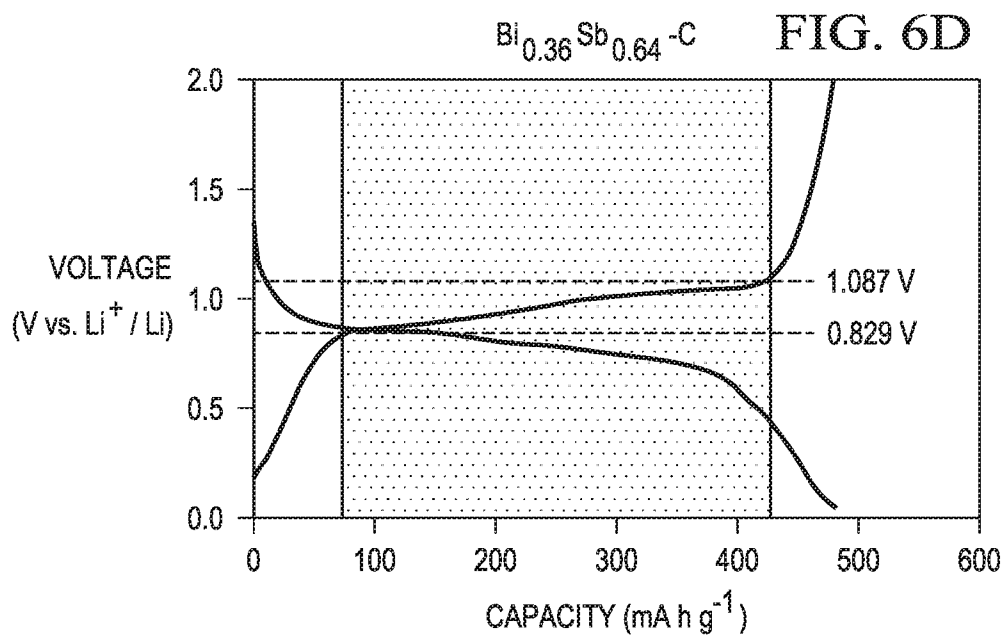
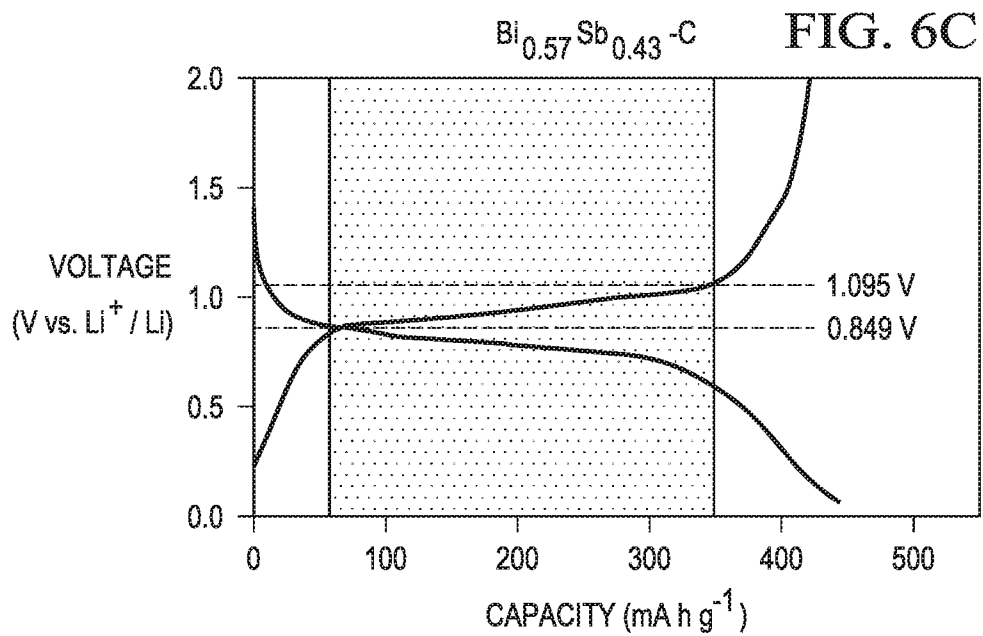


FIG. 5C



8/15



9/15

FIG. 6E

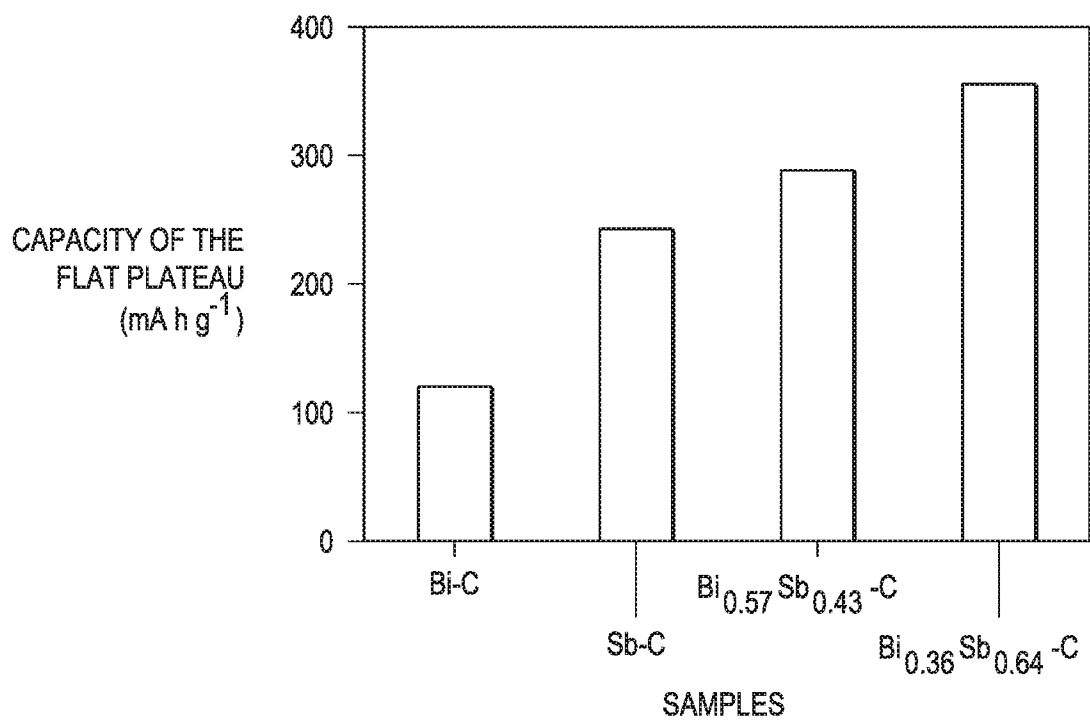
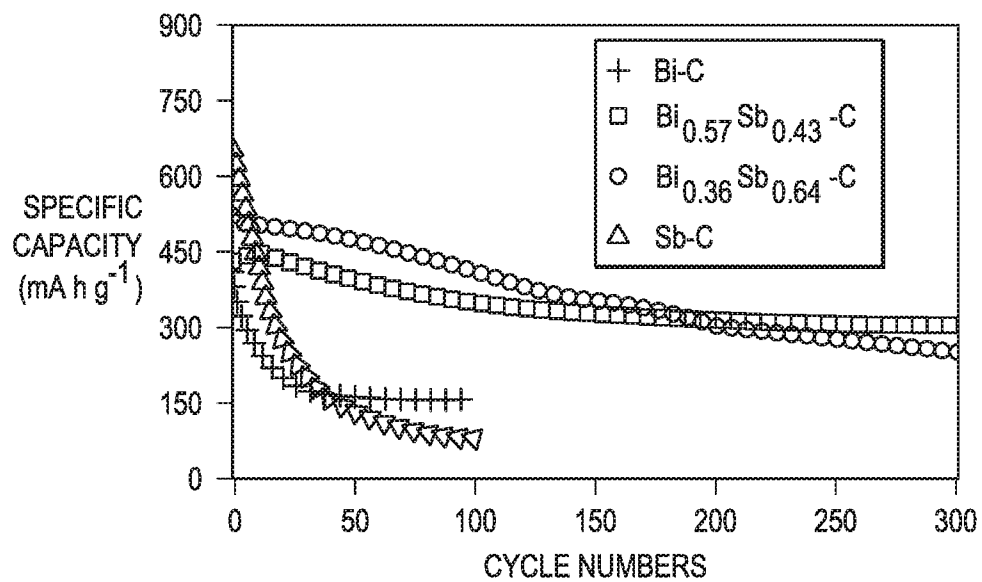


FIG. 7



10/15

FIG. 8A

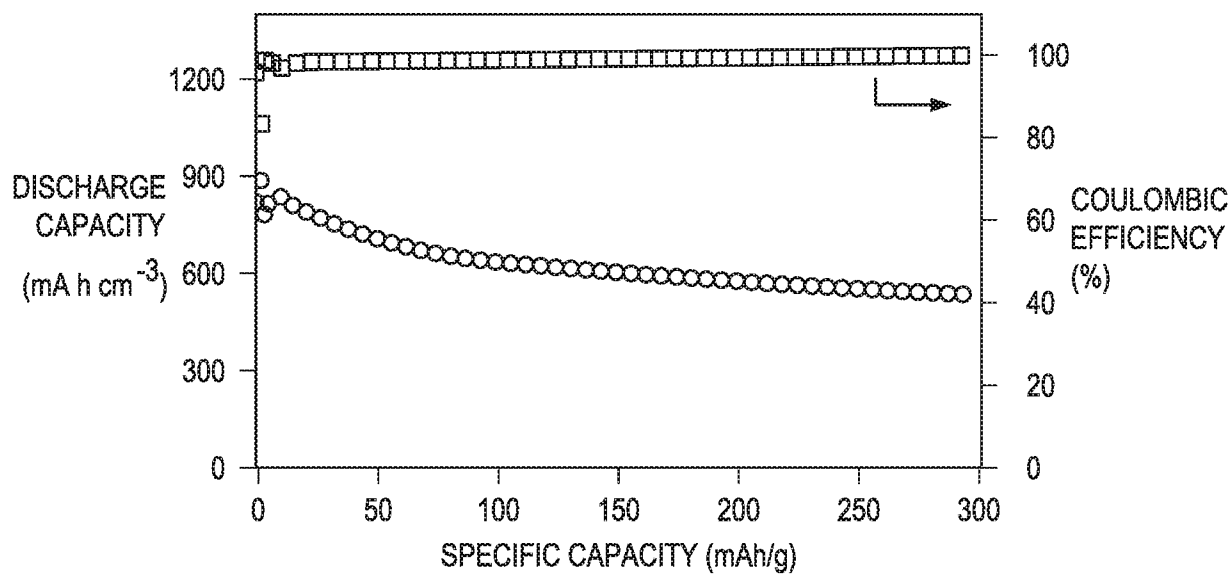
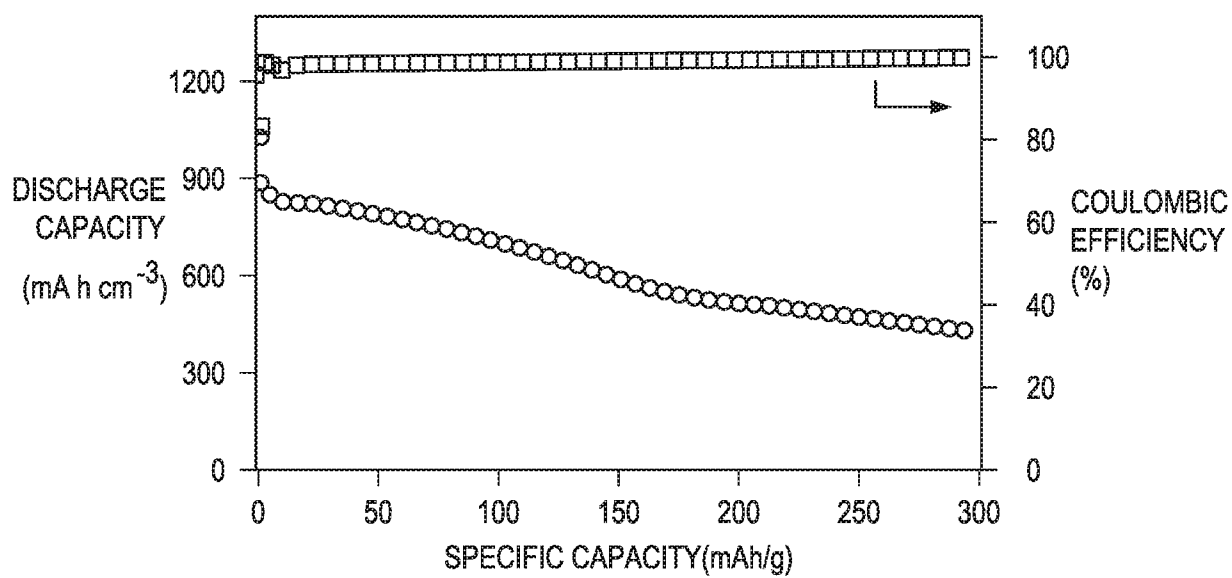


FIG. 8B



11/15

FIG. 9A

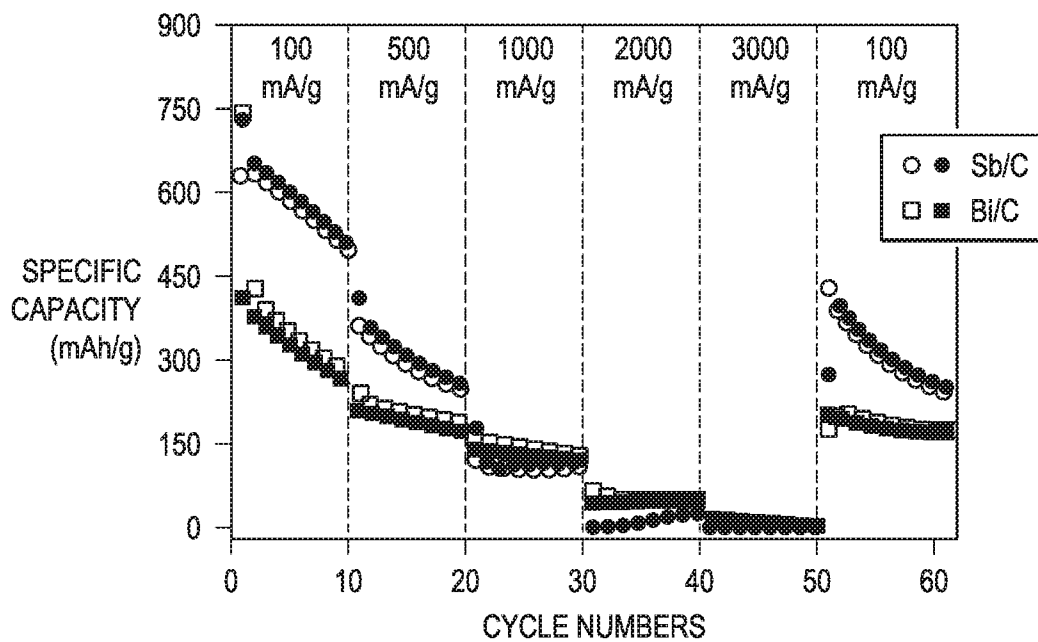
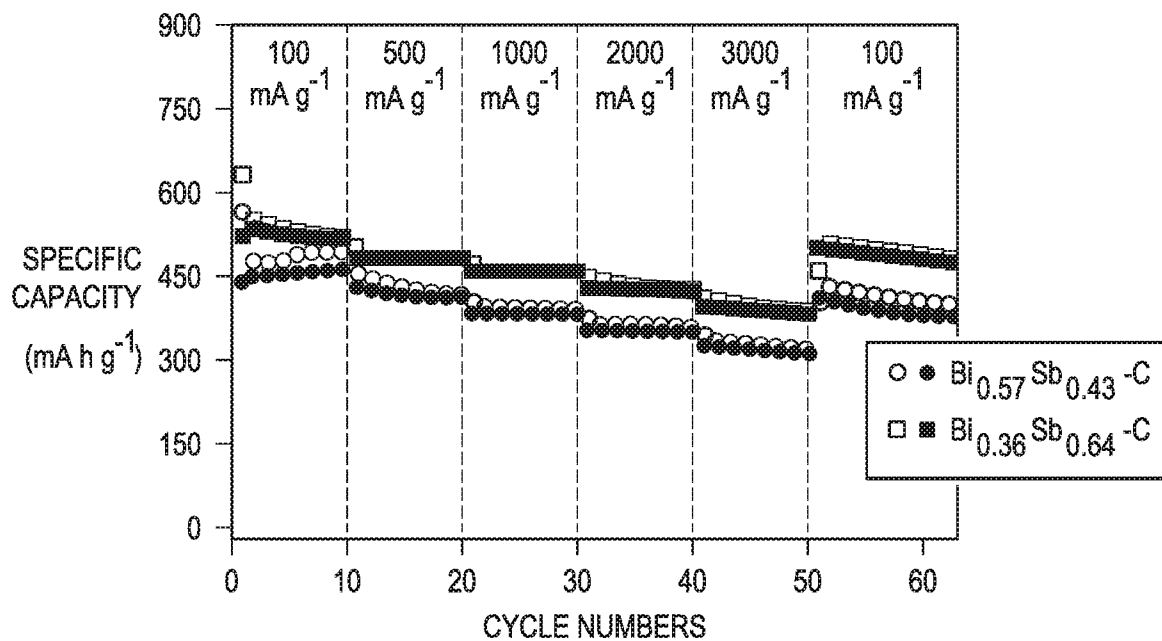


FIG. 9B



12/15

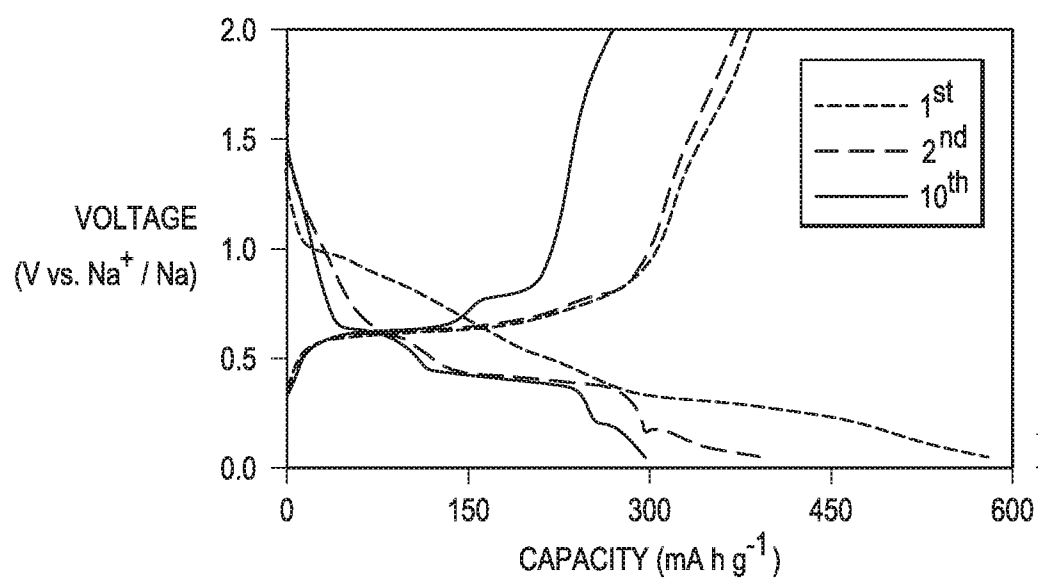


FIG. 10A

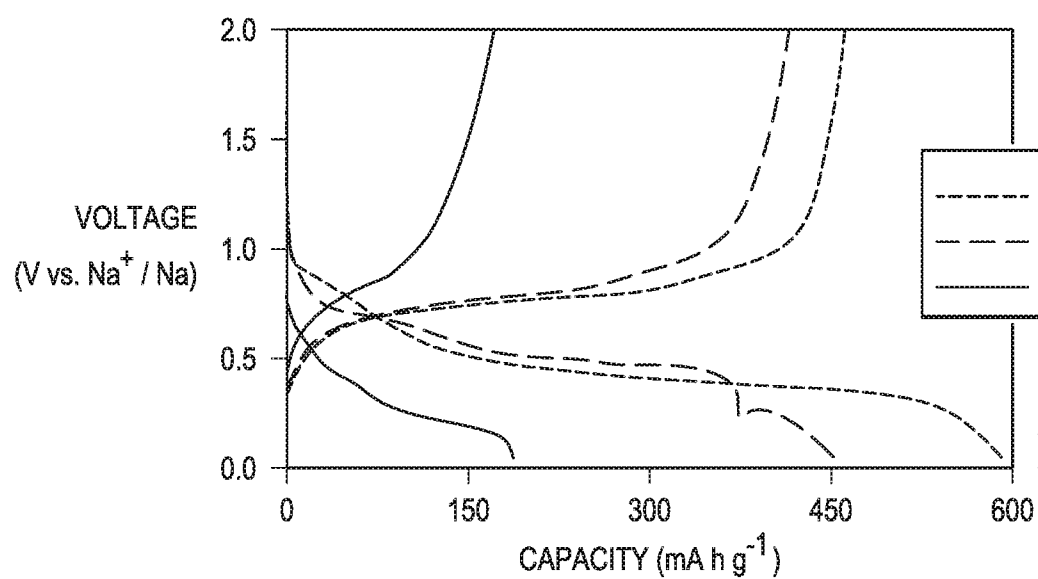


FIG. 10B

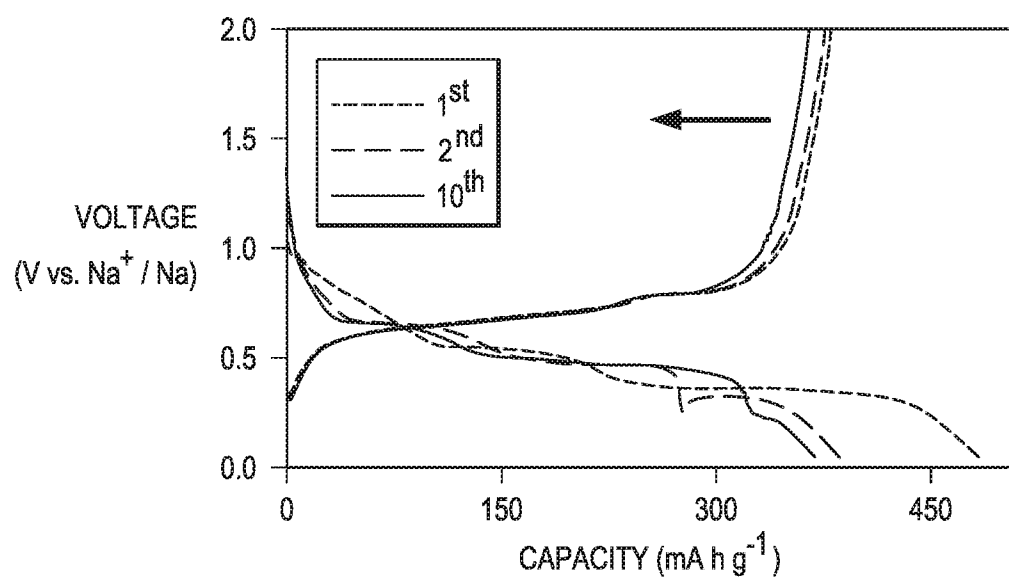


FIG. 10C

13/15

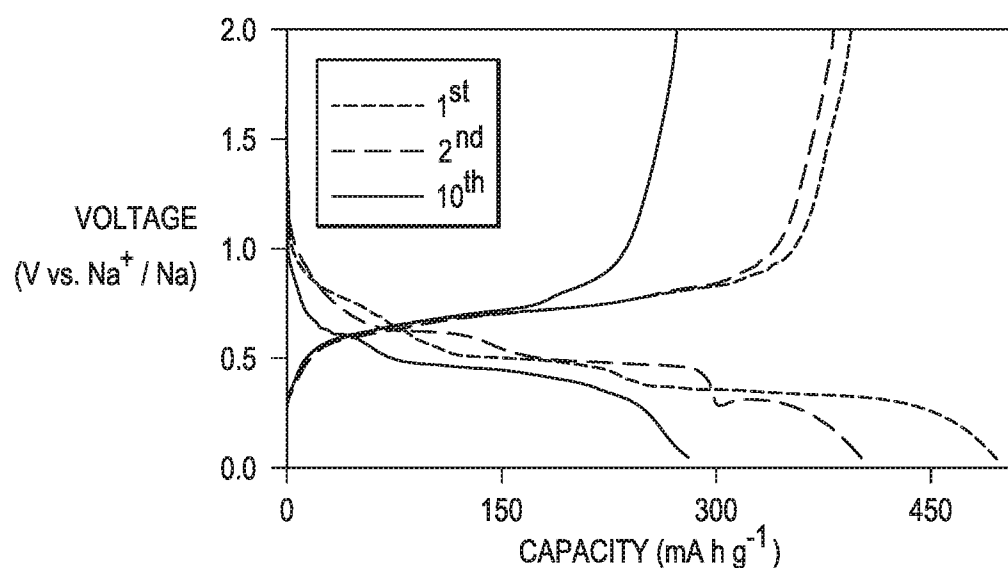


FIG. 10D

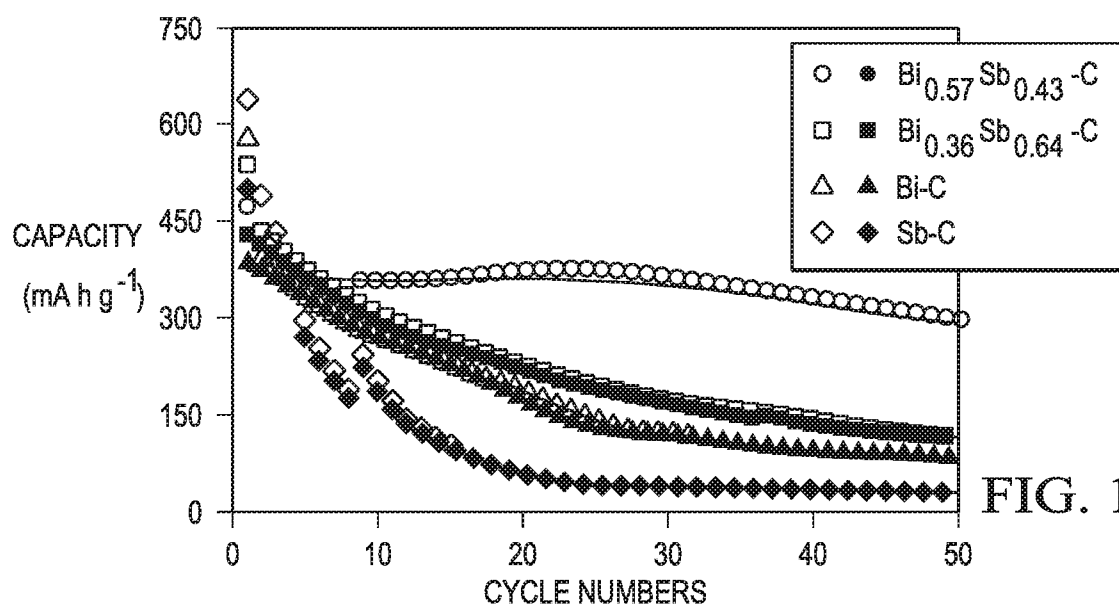


FIG. 11A

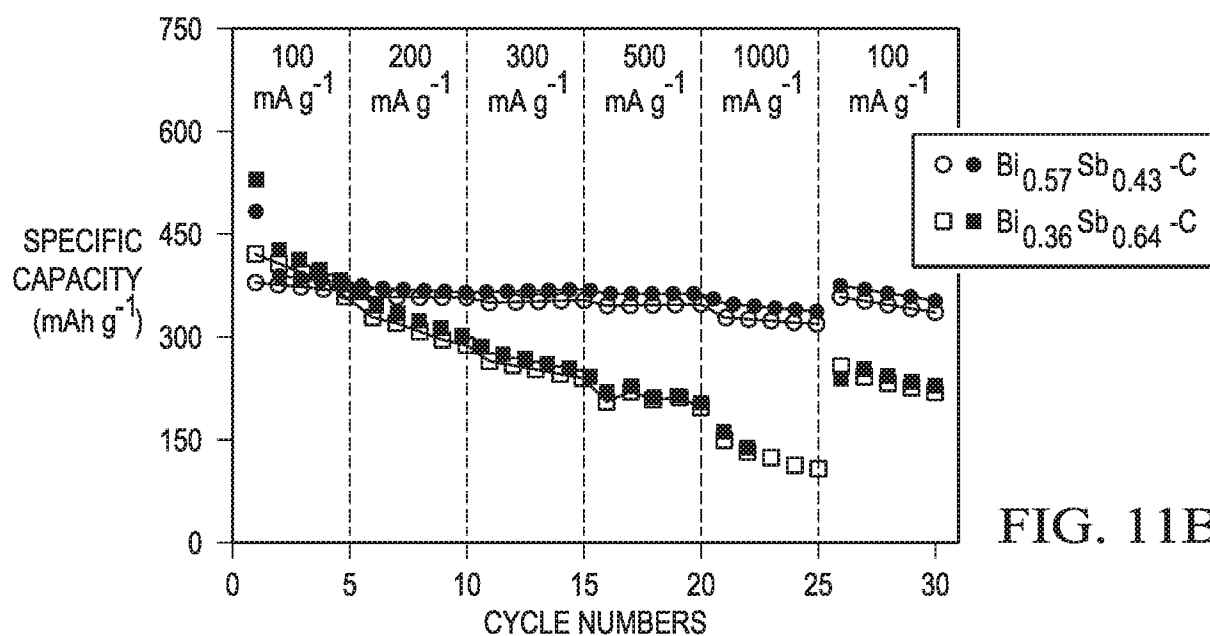


FIG. 11B

14/15

FIG. 12A

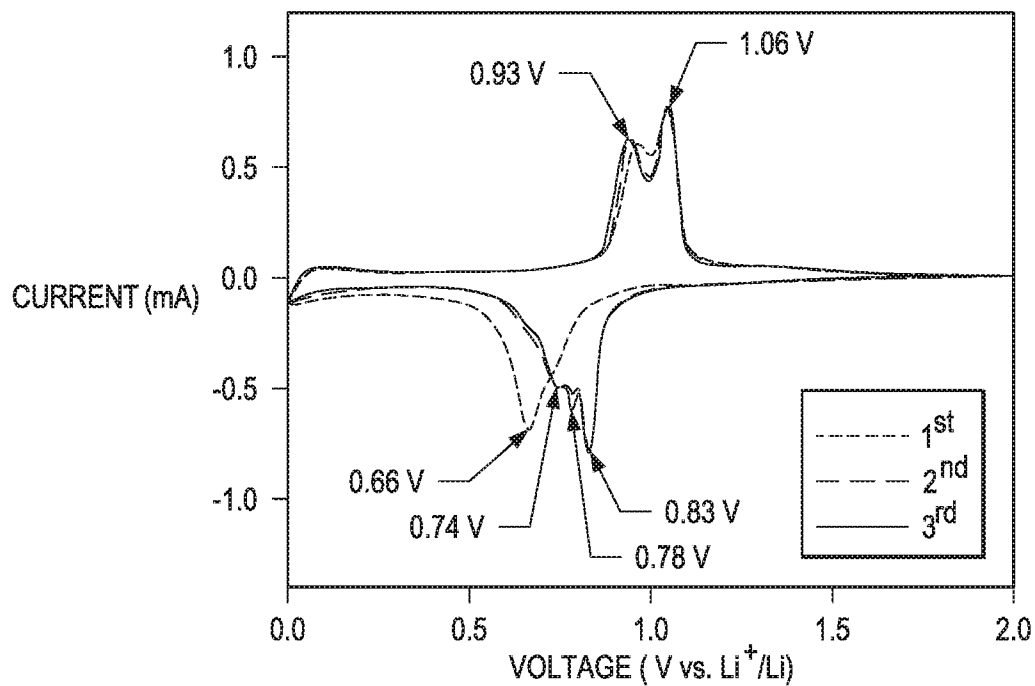
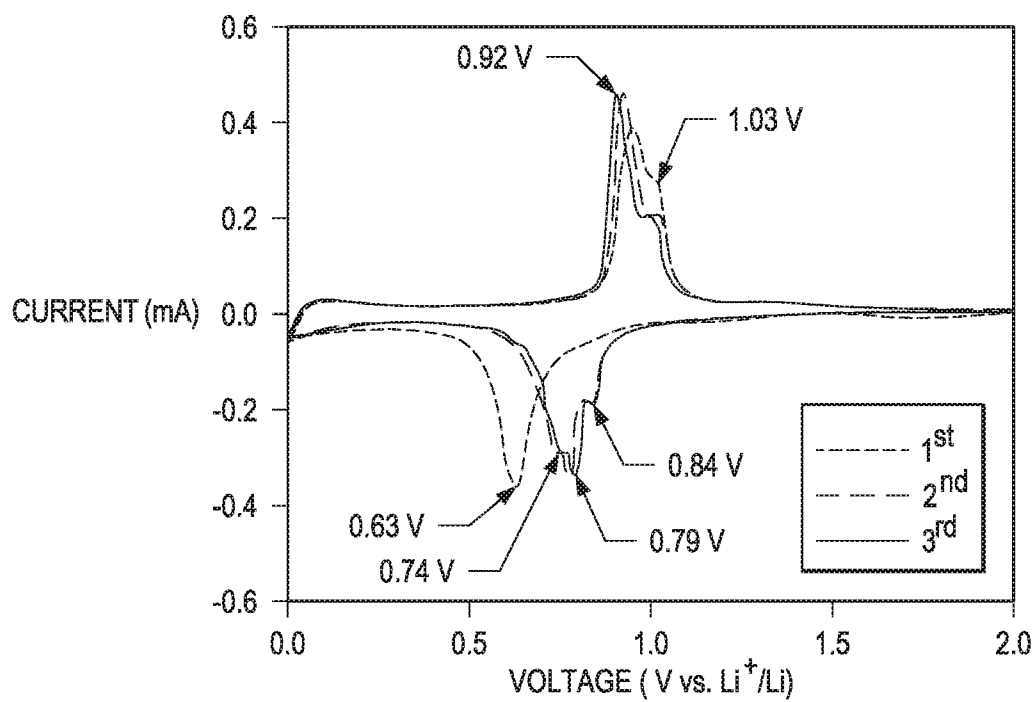


FIG. 12B



15/15

FIG. 12C

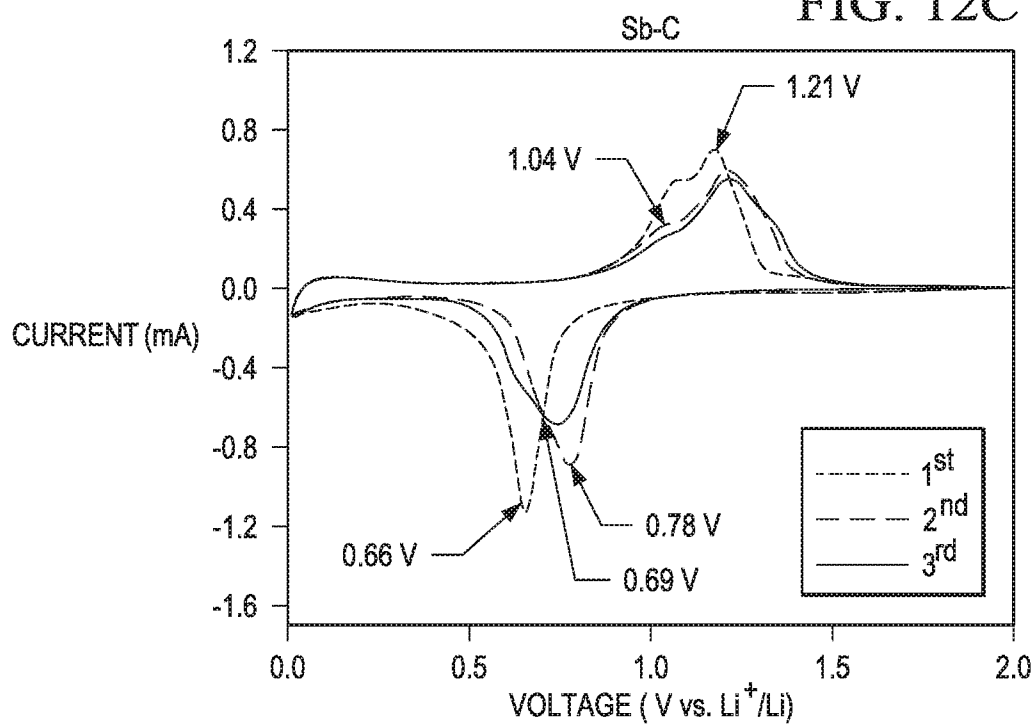
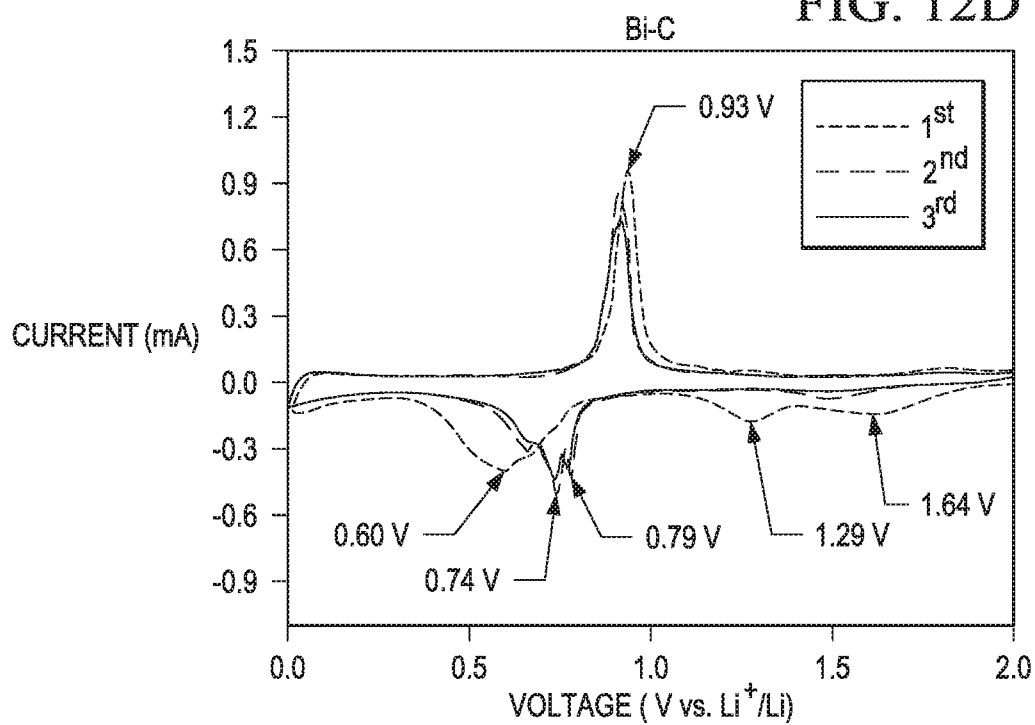


FIG. 12D



A. CLASSIFICATION OF SUBJECT MATTER**H01M 10/052(2010.01)i, H01M 10/054(2010.01)i, H01M 4/131(2010.01)i**

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

B. FIELDS SEARCHEDMinimum documentation searched (classification system followed by classification symbols)
H01M 10/052; B82B 1/00; B82B 3/00; H01M 4/02; H01M 4/58; H01M 10/054; H01M 4/131Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility modelsElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & keywords: Bi-Sb alloy, anode material, lithium ion battery, sodium ion battery, milling**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	JP 11-260369 A (MITSUBISHI CHEMICAL CORP.) 24 September 1999 See claim 1; paragraphs [0001], [0030]-[0032].	1-3, 13, 15-17, 30 4-12, 14, 18-29, 31-35
X	MIYAJIMA, MASAFUMI et al., "Synthesis of Bi-Sb Thermoelectric Material by Mechanical Alloying", Journal of the Japan Society of Powder and Powder Metallurgy, 1995, vol. 42, no. 2, pp. 146-150 See page 147.	33, 35
X	KR 10-1414536 B1 (INHA IND. PARTNERSHIP INST.) 4 July 2014 See claims 1, 3; paragraph [0001].	1-3, 13, 15-16, 30
X	ARTHUR, TIMOTHY S. et al., "Electrodeposited Bi, Sb and Bi _{1-x} Sb _x alloys as anodes for Mg-ion batteries", Electrochemistry Communications, 2012, vol. 16, pp. 103-106 See abstract; pages 103-104.	1-2
A	NULI, YANNA et al., "Synthesis and characterization of Sb/CNT and Bi/CNT composites as anode materials for lithium-ion batteries", Materials Letters, 2008, vol. 62, pp. 2092-2095 See page 2093.	1-35



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

04 May 2016 (04.05.2016)

Date of mailing of the international search report

04 May 2016 (04.05.2016)

Name and mailing address of the ISA/KR

International Application Division

Korean Intellectual Property Office

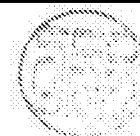
189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea

Facsimile No. +82-42-481-8578

Authorized officer

LEE, Dong Wook

Telephone No. +82-42-481-8163



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2016/014487Patent document
cited in search reportPublication
datePatent family
member(s)Publication
date

JP 11-260369A

24/09/1999

None

KR 10-1414536 B1

04/07/2014

KR 10-2014-0018569 A

13/02/2014