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(71) Applicant: **THE REGENTS OF THE UNIVERSITY OF CALIFORNIA** [US/US]; 1111 Franklin Street, 12th Floor, Oakland, California 94607-5200 (US).

(72) Inventor: **LIU, Gao**; c/o LAWRENCE BERKELEY NATIONAL LABORATORY, One Cyclotron Road M/S 90-R1116, Berkeley, California 94720-8127 (US).

(74) Agent: **CHIANG, Robin C.** et al.; LAWRENCE BERKELEY NATIONAL LABORATORY, Intellectual Property Office (IPO), Patent Group, One Cyclotron Road M/S 90-R1116, Berkeley, California 94720-8127 (US).

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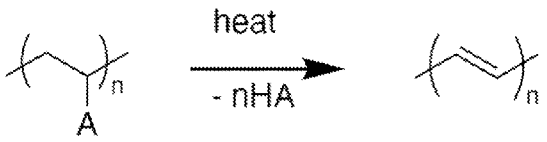
(54) Title: POLYMER CHARGE CONDUCTOR



Polyvinyl A

FIG. 4

(57) Abstract: The present invention provides for a polymer capable of conductance. In some embodiments, the polymer is useful in the manufacture of an electrical or electronic device, such as a battery.

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SUBSTITUTE SPECIFICATION – CLEAN COPY

Polymer charge conductor

Inventor: Gao Liu

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Patent Application Ser. No. 63/484,940, filed February 14, 2023, which is hereby incorporated by reference.

STATEMENT OF GOVERNMENTAL SUPPORT

[0002] The invention was made with government support under Contract No. DE-AC02-05CH11231 awarded by the U.S. Department of Energy. The government has certain rights in the invention.

FIELD OF THE INVENTION

[0003] This invention relates generally to polymers.

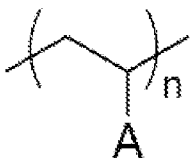
BACKGROUND OF THE INVENTION

[0004] Currently there is a need for a polymer capable of conductance for use as an electrode binder for Si, Sn, and/or graphite based anode electrodes for a lithium-ion or solid-state batteries.

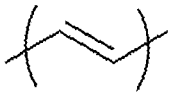
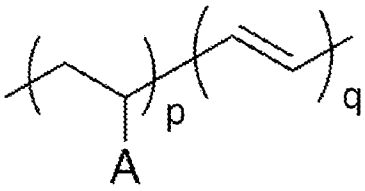
SUMMARY OF INVENTION

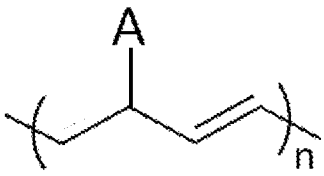
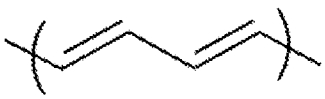
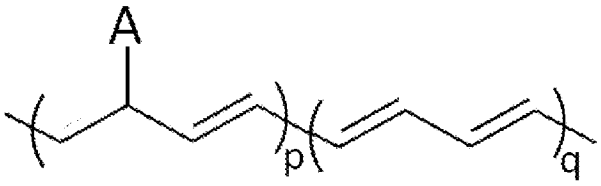
[0005] The present invention provides for a polymer capable of conductance. In some embodiments, the polymer is useful in the manufacture of an electrical or electronic device, such as a battery.

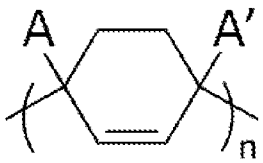
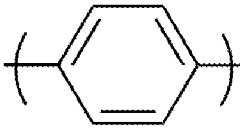
[0006] The present invention provides for a method of forming a conductive polymer, comprising (a) providing a polyvinyl polymer having the following chemical structure:

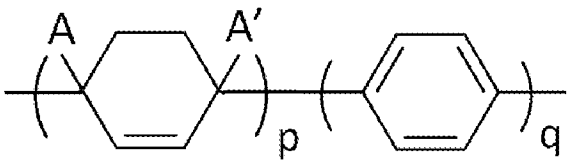


(I-a), wherein A is –OH, –OR, F, Cl, Br, I, $–SO_4R$, $–SO_3R$, $–NH_2$, $–NH_R$, $–NR_1R_2$, a phenyl, or a phenyl derivative, and R, R_1, and/or R_2 are each independently an

organic substituent; and (b) heating the polyvinyl polymer thereby forming at least one  to form the following chemical structure:  (I-b), wherein p has a value of $0 \leq p < 1$, q has a value of $0 < q \leq 1$, and $p + q = 1$.

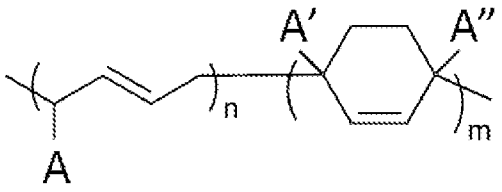
[0007] The present invention provides for a method of forming a conductive polymer, comprising (a) providing a precursor polymer having the following chemical structure:  (II-a), wherein A is –OH, –OR, F, Cl, Br, I, $–SO_4R$, $–SO_3R$, $–NH_2$, $–NH_R$, $–NR_1R_2$, a phenyl, or a phenyl derivative, and R, R_1, and/or R_2 are each independently an organic substituent; and (b) heating the precursor polymer thereby forming at least one  to form the following chemical structure:  (II-b), wherein p has a value of $0 \leq p < 1$, q has a value of $0 < q \leq 1$, and $p + q = 1$.

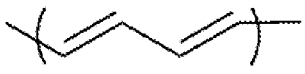
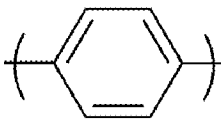
[0008] The present invention provides for a method of forming a conductive polymer, comprising (a) providing a precursor polymer having the following chemical structure:  (III-a), wherein A and A' are each independently –OH, –OR, F, Cl, Br, I, $–SO_4R$, $–SO_3R$, $–NH_2$, $–NH_R$, $–NR_1R_2$, a phenyl, or a phenyl derivative, and R, R_1, and/or R_2 are each independently an organic substituent; and (b) heating the precursor polymer thereby forming at least one  to form the following chemical structure:

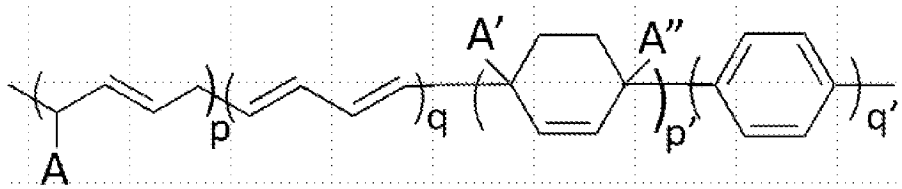


(III-b), wherein p has a value of $0 \leq p < 1$, q has a value of $0 < q \leq 1$, and $p + q = 1$.

[0009] The present invention provides for a method of forming a conductive polymer, comprising (a) providing a precursor polymer having the following chemical structure:



(IV-a), wherein A, A', and A" are each independently –OH, –OR, F, Cl, Br, I, $–SO_4R$, $–SO_3R$, $–NH_2$, $–NH_R$, $–NR_1R_2$, a phenyl, or a phenyl derivative, and R, R_1, and/or R_2 are each independently an organic substituent, n has a value of $0 < n < 1$, m has a value of $0 < m < 1$, and $n + m = 1$; and (b) heating the precursor polymer thereby forming at least one  and at least one  to form the following chemical structure:



(IV-b), wherein p has a value of $0 \leq p < n$, q has a value of $0 < q \leq n$, p' has a value of $0 \leq p' < m$, q' has a value of $0 < q' \leq m$, $p + q = n$, $p' + q' = m$, and $p + q + p' + q' = 1$.

[0010] In some embodiments, p has a value of $0 \leq p \leq 0.9$ and q has a value of $0.1 \leq q \leq 1$. In some embodiments, p has a value of $0 \leq p \leq 0.8$ and q has a value of $0.2 \leq q \leq 1$. In some embodiments, p has a value of $0 \leq p \leq 0.7$ and q has a value of $0.3 \leq q \leq 1$. In some embodiments, p has a value of $0 \leq p \leq 0.6$ and q has a value of $0.4 \leq q \leq 1$. In some embodiments, p has a value of $0 \leq p \leq 0.5$ and q has a value of $0.5 \leq q \leq 1$. In some embodiments, p has a value of $0 \leq p \leq 0.4$ and q has a value of $0.6 \leq q \leq 1$. In some embodiments, p has a value of $0 \leq p \leq 0.3$ and q has a value of $0.7 \leq q \leq 1$. In some

embodiments, p has a value of $0 \leq p \leq 0.2$ and q has a value of $0.8 \leq q \leq 1$. In some embodiments, p has a value of $0 \leq p \leq 0.1$ and q has a value of $0.9 \leq q \leq 1$. In some embodiments, p is 0 and q is 1.

[0011] For chemical structure (IV-b), n is about 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, or less than 100%, or a percentage within a range of any two preceding percentages, and m is about 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, or less than 100%, or a percentage within a range of any two preceding percentages. For chemical structure (IV-b), n is about 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, or less than 100%, or a percentage within a range of any two preceding percentages, and m is about 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, or less than 100%, or a percentage within a range of any two preceding percentages.

[0012] For chemical structure (IV-b), p is about 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, or less than 100% of n, or a percentage within a range of any two preceding percentages, and q is about 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, or less than 100% of n, or a percentage within a range of any two preceding percentages.

[0013] For chemical structure (IV-b), p' is about 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, or less than 100% of m, or a percentage within a range of any two preceding percentages, and q' is about 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, or less than 100% of m, or a percentage within a range of any two preceding percentages.

[0014] In some embodiments, the method further comprises adding an acid or base to the polyvinyl polymer to form a mixture prior to the heating step (b). In some embodiments, the acid or base added to the polyvinyl polymer is 0.0001% to 99.9% by weight of the mixture. In some embodiments, the base is a base listed in Table 1. In some embodiments, the method comprises adding a base to the polyvinyl polymer to form a mixture prior to the heating step (b), wherein the base is LiOH, NaOH, KOH, RbOH, CsOH, $Mg(OH)_2$, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$, or a mixture thereof. In some embodiments, the acid is an acid listed in Table 2. In some embodiments, the method comprises adding an acid to the polyvinyl polymer to form a mixture prior to the heating step (b), wherein the acid is H_2SO_4, H_3PO_4, HNO_3, HCl, HBr, HI, HPF_6, HTFSI. HFSI, $NClO_4$, $HBrO_4$, HIO_4, or a mixture thereof.

[0015] Table. 1. Suitable base.

Name	Formula	Name	Formula
Aluminum Hydroxide	Al(OH)3	Ammonium Hydroxide	NH4OH
Arsenic Hydroxide	As(OH)3	Barium Hydroxide	Ba(OH)2
Berylium Hydroxide	Be(OH)2	Bismuth (III) Hydroxide	Bi(OH)2
Boron Hydroxide	B(OH)3	Cadmium Hydroxide	Cd(OH)2
Calcium Hydroxide	Ca(OH)2	Cerium (III) Hydroxide	Ce(OH)3
Cesium Hydroxide	CsOH	Chromium (II) Hydroxide	Cr(OH)2
Chromium (III) Hydroxide	Cr(OH)3	Chromium (V) Hydroxide	Cr(OH)5
Chromium (VI) Hydroxide	Cr(OH)6	Cobalt (II) Hydroxide	Co(OH)2
Cobalt (III) Hydroxide	Co(OH)3	Copper (I) Hydroxide	CuOH
Copper (II) Hydroxide	Cu(OH)2	Gallium (II) Hydroxide	Ga(OH)2
Gallium (III) Hydroxide	Ga(OH)3	Gold (I) Hydroxide	AuOH
Gold (III) Hydroxide	Au(OH)3	Indium (I) Hydroxide	InOH
Indium (II) Hydroxide	In(OH)2	Indium (III) Hydroxide	In(OH)3
Irdium (III) Hydroxide	Ir(OH)3	Iron (II) Hydroxide	Fe(OH)2
Iron (III) Hydroxide	Fe(OH)3	Lanthanum Hydroxide	La(OH)3
Lead (II) Hydroxide	Pb(OH)2	Lead (IV) Hydroxide	Pb(OH)4
Lithium Hydroxide	LiOH	Magnesium Hydroxide	Mg(OH)2
Manganese (II) Hydroxide	Mn(OH)2	Manganese (III) Hydroxide	Mn(OH)3
Manganese (VI) Hydroxide	Mn(OH)4	Manganese (VII) Hydroxide	Mn(OH)7
Mercury (I) Hydroxide	Hg2(OH)2	Mercury (II) Hydroxide	Hg(OH)2
Molybdenum Hydroxide	Mo(OH)3	Neodymium Hydroxide	Nd(OH)3
Nickel Oxo-Hydroxide	NiOOH	Nickel (II) Hydroxide	Ni(OH)2
Nickel (III) Hydroxide	Ni(OH)3	Niobium Hydroxide	Nb(OH)3
Osmium (IV) Hydroxide	Os(OH)4	Palladium (II) Hydroxide	Pd(OH)2
Palladium (IV) Hydroxide	Pd(OH)4	Platinum (II) Hydroxide	Pt(OH)2
Platinum (IV) Hydroxide	Pt(OH)4	Plutonium (IV) Hydroxide	Pu(OH)4
Potassium Hydroxide	KOH	Radium Hydroxide	Ra(OH)4
Rubidium Hydroxide	RbOH	Ruthenium (III) Hydroxide	Ru(OH)3
Scandium Hydroxide	Sc(OH)3	Silicon Hydroxide	Si(OH)4
Silver Hydroxide	AgOH	Sodium Hydroxide	NaOH
Strontium Hydroxide	Sn(OH)2	Tantalum (V) Hydroxide	Ta(OH)5
Technetium (II) Hydroxide	Tc(OH)2	Tetramethylammonium Hydroxide	C4H12NOH
Thallium (I) Hydroxide	TlOH	Thallium (III) Hydroxide	Tl(OH)3
Thorium Hydroxide	Th(OH)4	Tin (II) Hydroxide	Sn(OH)2
Tin (IV) Hydroxide	Sn(OH)4	Titanium (II) Hydroxide	Ti(OH)2
Titanium (III) Hydroxide	Ti(OH)3	Titanium (IV) Hydroxide	Ti(OH)4
Tungsten (II) Hydroxide	W(OH)2	Uranyl Hydroxide	(UO2)2(OH)4
Vanadium (II) Hydroxide	V(OH)2	Vanadium (III) Hydroxide	V(OH)3
Vanadium (V) Hydroxide	V(OH)5	Ytterbium Hydroxide	Yb(OH)3
Yttrium Hydroxide	Y(OH)3	Zinc Hydroxide	Zn(OH)2
Zirconium Hydroxide	Zr(OH)4		

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[0016] Table. 2. Suitable acid.

Formula	Acid Name	Salt name	Formula	Acid Name	Salt name
H2SO3	Sulfurous Acid	Sulfite	H2SO4	Sulfuric Acid	Sulfate
H2SO2	Hyposulfurous Acid	Hyposulfite	H2SO5	Persulfuric Acid	Persulfate
H2S2O7	Pyrosulfuric Acid	Pyrosulfate	H2S2O5	Disulfurous Acid	Disulfite
H2S2O2	Thiosulfurous Acid	Thiosulfite	H2S	Hydrosulfuric Acid	Hydrosulfate
H2S2O8	Peroxydisulfuric Acid	Peroxydisulfate	HClO4	Perchloric Acid	Perchlorate
HCl	Hydrochloric Acid	Hydrochlorate	HClO	Hypochlorous Acid	Hypochlorite
HClO2	Chlorous Acid	Chlorite	HClO3	Chloric Acid	Chlorate
HNO	Hyponitrous Acid	Hyponitrite	HNO2	Nitrous Acid	Nitrite
HNO3	Nitric Acid	Nitrate	HNO4	Pernitric Acid	Pernitrate
H2CO2	Carbonous Acid	Carbonite	H2CO3	Carbonic Acid	Carbonate
H2CO	Hypocarbonous Acid	Hypocarbonite	H2CO4	Percarbonic Acid	Percarbonate
H2C2O4	Oxalic Acid	Oxalate	CH3COOH	Acetic Acid	Acetate
H3PO4	Phosphoric Acid	Phosphate	H3PO3	Phosphorous Acid	Phosphite
H3PO2	Hypophosphous Acid	Hypophosphite	H3PO5	Perphosphoric Acid	Perphosphate
H4P2O6	Hypophosphoric Acid	Hypophosphate	H4P2O7	Pyrophosphoric Acid	Pyrophosphate
H3P	Hydrophosphoric Acid	Hydrophosphate	HBr	Hydrobromic Acid	Hydrobromate
HBrO2	Bromous Acid	Bromite	HBrO3	Bromic Acid	Bromate
HBrO	Hypobromous Acid	Hypobromite	HIO	Hypoiodous Acid	Hypoiodite
HIO2	Iodous Acid	Iodite	HIO3	Iodic Acid	Iodate
HIO4	Periodic Acid	Periodate	HI	Hydroiodic Acid	Hydroiodate
HFO2	Fluorous Acid	Fluorite	HFO3	Fluoric Acid	Fluorate
HFO	Hypofluorous Acid	Hypofluorite	HFO4	Perfluoric Acid	Perfluorate
HF	Hydrofluoric Acid	Hydrofluorate	H2CrO4	Chromic Acid	Chromate
H2CrO3	Chromous Acid	Chromite	H2CrO2	Hypochromous Acid	Hypochromite
H2CrO5	Perchromic Acid	Perchromate	H2Se	Hydroselenic Acid	Hydroselenate
H2SeO4	Selenic Acid	Selenate	H2SeO3	Selenous Acid	Selenite
HN3	Hydronitric Acid	Hydronitrate	H3BO3	Boric Acid	Borate
H2MoO4	Molybdic Acid	Molydate	H4XeO6	Perxenic Acid	Perxenate
H2SiF6	Silicofluoric Acid	Silicofluorate	H6TeO6	Telluric Acid	Tellurate
H2TeO3	Tellurous Acid	Tellurite	H2WO4	Tungstic Acid	Tungstate
H2XeO4	Xenic Acid	Xenate	C6H8O7	Citric Acid	Citrate

HCOOH	Formic Acid	Formate	H4Sb2O7	Pyroantimonic Acid	Pyroantimonate
HMnO4	Permanganic Acid	Permanganate	H2MnO4	Manganic Acid	Manganate
HSbO3	Antimonic Acid	Antimonate	H3SbO3	Antimonous Acid	Antimonite
H2SiO3	Silicic Acid	Silicate	H2TiO3	Titanic Acid	Titanate
H3AsO4	Arsenic Acid	Arsenate	HTcO4	Pertechnetic Acid	Pertechnetate
H3As	Hydroarsenic Acid	Hydroarsenate	H2Cr2O7	Dichromic Acid	Dichromate
H2B4O7	Tetraboric Acid	Tetraborate	H2SnO3	Metastannic Acid	Metastannate
H2C2O2	Hypooxalous Acid	Hypooxalite	H3(F3(CN)6)	Ferricyanic Acid	Ferricyanate
HCNO	Cyanic Acid	Cyanate	H2SiO2	Silicous Acid	Silicite
HCN	Hydrocyanic Acid	Hydrocyanate	HSCN	Thiocyanate Acid	Thiocyanate
H2UO4	Uranic Acid	Uranate	H2U2O7	Diuranic Acid	Diuranate

List of Common Organic Acids

Formula	Acid Name	Salt name	Formula	Acid Name	Salt name
CH2(COOH)2	Malonic Acid	Malonate	H2C6H6O7	Citric Acid	Citrate
H2C4H4O6	Tartartic Acid	Tartartate	HC5H8NO4	Glutamic Acid	Glutamate
H2C8H4O4	Phthalic Acid	Phthalate	H2C9H14O4	Azelaic Acid	Azelate
HC4H3N2O3	Barbituric Acid	Barbiturate	HC14H11O3	Benzilic Acid	Benzilate
C9H8O2	Cinnamic Acid	Cinnamate	C4H4O4	Fumaric Acid	Fumarate
C5H8O4	Glutaric Acid	Glutarate	C6H12O7	Gluconic Acid	Gluconate
C5H11COOH	Hexanoic Acid	Hexanoate	HC3H5O3	Lactic Acid	Lactate
H2C4H4O5	Malic Acid	Malate	HC18H33O2	Oleic Acid	Oleate
C19H19N7O6	Folic Acid	Folate	HC2COOH	Propiolic Acid	Propiolate
C17H35COOH	Stearic Acid	Stearate	C76H53O46	Tannic Acid	Tannate
C2HF3O2	Trifluoroacetic Acid		H2C5H2N4O3	Uric Acid	Urate
HC6H7O6	Ascorbic Acid	Ascorbate	HC7H5O5	Gallic Acid	Gallate
HC9H7O4	Acetylsalicylic Acid		CH3COOH	Acetic Acid	Acetate

[0017] In some embodiments, the method further comprises doping the polymer having the chemical structure of (I-b), (II-b), (III-b), or (IV-b) with O_2, I_2, PF_6^-, or like anion, and/or metal cation, to further enhance electronic conductivity. In some embodiments, the metal cation is an alkali metal or alkaline earth metal cation. In some embodiments, the alkali metal cation is lithium ion, sodium ion, potassium ion, rubidium ion, caesium ion, or the like. In some embodiments, the alkaline earth metal cation is beryllium ion, magnesium ion, calcium ion, strontium ion, barium ion, or the like. In some embodiments, the chemical structure (I-b), (II-b), (III-b), (IV-b), or a mixture thereof, is in a thin film. In some embodiments, the method comprises passing an electric current through chemical structure (I-b), (II-b), (III-b), (IV-b), or a mixture thereof.

[0018] The present invention provides for an electrically conductive composition comprising one or more polymers, wherein each polymer has the chemical structure of (I-b), (II-b), (III-b), (IV-b), or a mixture thereof.

[0019] The present invention provides for an electric device comprising an electric circuit comprising the composition a chemical structure of (I-b), (II-b), (III-b), (IV-b), or a mixture thereof, wherein an electric current is pass through the chemical structure of (I-b), (II-b), (III-b), (IV-b), or a mixture thereof. In some embodiments, the one or more polymers are electrode binders with electrode materials. In some embodiments, the conductive polymers are used as conductive electrode binders with electrode materials to form electrode for battery applications.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] The foregoing aspects and others will be readily appreciated by the skilled artisan from the following description of illustrative embodiments when read in conjunction with the accompanying drawings.

[0021] Fig. 1. From polybutadiene to synthesize polyhydroxybutadiene to thermal formation of polyacetylene

[0022] Fig. 2. From cyclohexdiene to synthesize polycyclodihydroxyhexene to thermal

formation of polyphenylene

[0023] Fig. 3. From polybutadiene-cyclohexene to synthesize polyhydroxybutadiene-cyclodihydroxyhexene to thermal formation of polyacetylene-phenylene

[0024] Fig. 4. When the depolymerization and decomposition are controlled, the thermal treatment of "polyvinyl A" leads to formation of polyacetylene conductive polymer. A: OH, OAc, F, Cl, Br, I, OCH_3, SO_4R, SO_3R, NH_2, NHR, NR_1R_2, phenyl and/or phenyl derivatives. R, R_1, R_2 can be any organic groups.

[0025] Fig. 5. Partial elimination of HA of "polyvinyl A" leads to formation of polyacetylene conductive polymer with functional A groups in the polymer structure. A: OH, OAc, F, Cl, Br, I, OCH_3, SO_4R, SO_3R, NH_2, NHR, NR_1R_2, phenyl and/or phenyl derivatives. R, R_1, R_2 can be any organic groups. In order to promote the formation of more polyacetylene structure, and less decomposition during heating process. A base or acid can be added to the polyvinyl A, before heating process. The added acid or base can facilitate lower temperature HA elimination, and prevent polymer from structure decomposition. The added acid or base among ranging from 0.0001% to 99.9% by weight to the polyvinyl A mixture. Base choices: LiOH, NaOH, KOH, RbOH, CsOH, $Mg(OH)_2$, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$, ammonia (NH3 or NH4.OH), amines and its derivatives such as triethylamine, and nitrogen based organic base such as 1,5-Diazabicyclo(4.3.0)non-5-ene (DBN), etc., both strong and weak bases. Acid choices: H_2SO_4, H_3PO_4, HNO_3, HCl, HBr, HI, HPF_6, HTFSI, HFSI, $HClO_4$, $HBrO_4$, HIO_4, Acetic acid (HAC), citric acid ($C_6H_8O_7$), H2SO3, HF, H2S, etc., both strong and week acids. A: OH, OAc, F, Cl, Br, I, OCH_3, SO_4R, SO_3R, NH_2, NHR, NR_1R_2, phenyl and/or phenyl derivatives. R, R_1, R_2 can be any organic groups.

[0026] Fig. 6. Polyvinyl alcohol full elimination without decomposition. Weight loss: 40.9%; weight remaining: 59.1%.

[0027] Fig. 7. Polyvinyl alcohol partial elimination of H_2O without decomposition lead to higher remaining weight. Weight remaining > 59.1%. Partial elimination of OH group of polyvinyl alcohol leads to formation of polyacetylene conductive polymer with functional OH groups in the polymer structure. This OH groups can provide functions such as adhesion or enhance mechanical strength. Fig. 8. Polyvinyl alcohol partial elimination of H_2O without

decomposition lead to higher remaining weight. Weight remaining > 59.1%. In order to promote the formation of more polyacetylene structure, and less decomposition during heating process. A base or acid can be mixed to the polyvinyl alcohol, before heating process. The added acid or base can facilitate lower temperature H2O elimination, and prevent polymer chain from structure decomposition. The added acid or base among ranging from 0.0001% to 99.9% by weight to the polyvinyl alcohol mixture. By control the thermal process, different number of OH groups can be retained in the polymer to provide adhesion, and overall mechanical strength. The thermal treatment can be done in ambient air condition, or inert atmosphere such as N2 and Ar gas environment or in reduced pressure to vacuum. When heating in air, some remaining hydroxyl groups can also be oxidized to carbonyl groups to adjust the bandgap of the pi-pi conjugation to promote more n-doping at higher potential. Base choices: LiOH, NaOH, KOH, RbOH, CsOH, $Mg(OH)_2$, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$,ammonia (NH3 or NH4.OH), amines and its derivatives such as triethylamine, and nitrogen based organic base such as 1,5-Diazabicyclo(4.3.0)non-5-ene (DBN), etc., both strong and weak bases. Acid choices: H_2SO_4, H_3PO_4, HNO_3, HCl, HBr, HI, HPF_6, HTFSI, HFSI, $HClO_4$, $HBrO_4$, HIO_4, Acetic acid (HAC), citric acid ($C_6H_8O_7$), H2SO3, HF, H2S, etc., both strong and week acids. Polyvinyl alcohol partial elimination of H_2O without decomposition lead to higher remaining weight. Weight remaining > 59.1%. In order to promote the formation of more polyacetylene structure, and less decomposition during heating process. A base or acid can be added to the polyvinyl alcohol, such as, NaOH, or H2SO4 at 1% to 40% by weight ratio before heating process at Ar atmosphere. The base or acid added PVA shows lower temperature H_2O elimination and prevent from structure decomposition. When heating in air, some remaining hydroxyl groups can also be oxidized to carbonyl groups to adjust the bandgap of the pi-pi conjugation to promote more n-doping at higher potential.

[0028] Fig. 8. Heating scan rate all at 0.2 °C/min, experiment done in Argon (Ar) atmosphere. PVA: Pure. PVA 1% NaOH: PVA with 1% weight of NaOH solution, PVA:NaOH=10:3 by weight. PVA H_2SO_4: PVA with 1% weight of H_2SO_4 solution, PVA:H_2SO_4=10:3.

[0029] Fig. 9. TGA experiment done in Ar atmosphere. PVA with 1% weight of NaOH solution, PVA:NaOH=10:3 by weight. Theoretical weight retention is 68%

[0030] Fig. 10. TGA experiment done in Ar atmosphere. PVA with 1% weight of NaOH solution, PVA:NaOH=10:3 by weight. Theoretical weight retention is 68%

[0031] Fig. 11. TGA experiment done in Ar atmosphere. PVA with 2% weight of NaOH solution, PVA:NaOH=5:3 by weight. Theoretical weight retention is 74%

[0032] Fig. 12. TGA experiment done in Ar atmosphere of Pure PVA, and retrieve sample after heating to 240 ° C and cool down to ambient temperature.

[0033] Fig. 13. TGA experiment done in Ar atmosphere, and retrieve sample after heating to 240 ° C and cool down to ambient temperature. PVA with 0.5% weight of NaOH solution, PVA:NaOH=20:3 by weight. Weight retention is 64%.

[0034] Fig. 14. TGA experiment done in Ar atmosphere, and retrieve sample after heating to 240 ° C and cool down to ambient temperature. PVA with 1% weight of NaOH solution, PVA:NaOH=10:3 by weight. Weight retention is 68%.

[0035] Fig. 15. TGA experiment done in Ar atmosphere, and retrieve sample after heating to 240 ° C and cool down to ambient temperature. PVA with 2% weight of NaOH solution, PVA:NaOH=5:3 by weight. Weight retention is 74%.

[0036] Fig. 16. FTIR spectra of the TGA treated PVA samples in Ar atmosphere at different NaOH concentrations and heating rates, and stopped at 240 °C. 0.5% NaOH is PVA:NaOH = 20:3 by weight. 1% NaOH is PVA: NaOH = 10:3. At 2% NaOH is PVA: NaOH = 5:3. Heating rates: Pure PVA, 250 °C, 0.2 °C/min; PVA0.5NaOH, 250 °C, 0.5% NaOH, 12 °C/min; PVA1NaOH, 250 °C, 1% NaOH, 6 °C/min; PVA2NaOH, 250 °C, 2% NaOH, 3 °C/min.

[0037] Fig. 17. Detailed FTIR spectra from Fig. 16.

[0038] Fig. 18. PVA:NaOH and Si electrode treated in Ar - SiPN240 cycling data.

[0039] Fig. 19. PVA and Si electrode treated in Ar - SiP240 cycling data.

[0040] Fig. 20. (A) The electrode of SiPN240 can be lithiated to almost full capacity. This electrode is made with PVA:NaOH 10:1 water solution with Si. (B) The electrode of SiP240

cannot be lithiated. This electrode is made with PVA 10% water solution with Si.

DETAILED DESCRIPTION OF THE INVENTION

[0041] Before the invention is described in detail, it is to be understood that, unless otherwise indicated, this invention is not limited to particular sequences, expression vectors, enzymes, host microorganisms, or processes, as such may vary. It is also to be understood that the terminology used herein is for purposes of describing particular embodiments only and is not intended to be limiting.

[0042] In this specification and in the claims that follow, reference will be made to a number of terms that shall be defined to have the following meanings:

[0043] The terms "optional" or "optionally" as used herein mean that the subsequently described feature or structure may or may not be present, or that the subsequently described event or circumstance may or may not occur, and that the description includes instances where a particular feature or structure is present and instances where the feature or structure is absent, or instances where the event or circumstance occurs and instances where it does not.

[0044] As used in the specification and the appended claims, the singular forms "a," "an," and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "molecules" includes a plurality of a molecule species as well as a plurality of molecules of different species.

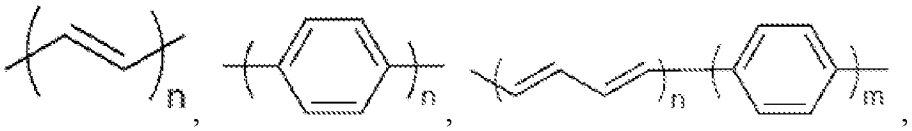
[0045] Where a range of values is provided, it is understood that each intervening value, to the tenth of the unit of the lower limit unless the context clearly dictates otherwise, between the upper and lower limits of that range is also specifically disclosed. Each smaller range between any stated value or intervening value in a stated range and any other stated or intervening value in that stated range is encompassed within the invention. The upper and lower limits of these smaller ranges may independently be included or excluded in the range, and each range where either, neither or both limits are included in the smaller ranges is also encompassed within the invention, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or

both of those included limits are also included in the invention.

[0046] The term "about" refers to a value including 10% more than the stated value and 10% less than the stated value.

[0047] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, the preferred methods and materials are now described. All publications mentioned herein are incorporated herein by reference to disclose and describe the methods and/or materials in connection with which the publications are cited.

[0048] In some embodiments, the polymer formed has the following chemical structure:



,

,

or 

; wherein n, m, or x are independently any number from 5, 10, 50, 100, 500, 1000, 5000, 10000, 50000, 1000000, or any number with a range of any of two preceding numbers; A is –OH, –OAc, F, Cl, Br, I, –OCH_3, $–SO_4R$, $–SO_3R$, $–NH_2$, –NHR, $–NR_1R_2$, phenyl and/or phenyl derivatives; and R, R_1, and/or R_2 are each independently any organic groups.

[0049] Herein describes chemistries and procedures to synthesize the polymer of the present invention, and functional polymer dual charge (ion and electron) conductors comprising the polymer of the present invention. These procedures use low cost starting materials, and low cost procedures.

[0050] The polymer of the present invention can be used as an electrode binder for Si, Sn,

and/or graphite based anode electrode for a lithium-ion or solid-state battery.

[0051] The present invention provides for an electrical or electronic device, such as a battery comprising the polymer of the present invention, or a electrode comprising the polymer of the present invention.

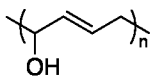
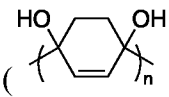
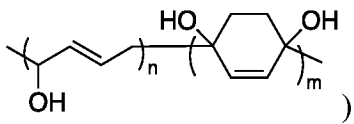
[0052] The polymer of the present invention can be built into pouch cells to test the performance of the polymers.

[0053] The polymer of the present invention can be used in both consumer electronic battery and electric vehicle battery. Unlike regular binder, which is not conductive, this polymer binder is both electrically and ionically conducting, as well as provide adhesion.

[0054] The present invention provides for a method of synthesizing the polymer of the present invention comprising step(s) described herein.

[0055] The electrodes and/or devices, or methods, of the present invention can further comprise element(s), component(s), or step(s) described in U.S. Provisional Patent Application Ser. No. 63/369,182, filed July 22, 2022, and PCT International Patent Application No. PCT/US2023/028482, filed July 24, 2023, both titled "Mixed solid-state ionic-electronic polymer conductors for electrochemical devices", both of which are hereby incorporated by reference.

[0056] The following provides for examples of the polymers of the present invention, and methods for synthesizing thereof:

[0057] The present invention provides for a mixture comprising A and B, wherein A is a polyvinylalcohol (PVA), polyhydroxybutadiene (), polycyclodihydroxyhexene () or polyhydroxybutadiene-cyclodihydroxyhexene (); and B is a base or acid.

[0058] In some embodiments, the base is a compound listed in Table 1. In some embodiments, the base is a metal carbonate salt (such as, Na_2CO_3 or $NaHCO_3$), a phosphate

salt (such as, Na_3PO_4 or Na_2HPO_4), or an organic base (such as Ammonia, Methylamine, Ethylamine, Diethylamine, Triethylamine, Hydroxylamine, Hydrazine, Aniline, Pyridine, and the like; or an organic superbase, such as a phosphazene, phosphane, amidine, and/or guanidines), or a mixture thereof.

[0059] In some embodiments, the acid is a compound listed in Table 2.

[0060] In some embodiments, B comprises from about 0.001% to about 99% by weight of the mixture.

[0061] The present invention provides for a method of making the mixture, comprising: (a) mixing A in water solution and B in water solution to form a mixture solution, and (b) optionally drying the mixture solution at an ambient or room temperature to separate water from the the mixture of A and B.

[0062] In some embodiments, the method comprises one or more of the folowing steps: (1) Heating said mixture at the inert atmosphere to a range of about 50 - 800 °C at a time period of about 1 second to 48 hours, and cool down to ambient temperature to produce electrically conductive polymer. The heating range can further narrow down to about 150 - 250 °C over a period of about 1 hour. (2) Heating said mixture at ambient air condition to a range of about 50 - 800 °C at a time period of about 1 second to 48 hours, and cool down to ambient temperature to produce electrically conductive polymer. The heating range can further narrow down to about 150 - 250 °C over a period of about 1 hour. (3) The mixture solution is combined with lithium ion battery electrode materials, such as carbon, Si, SiOx, or Sn particles to make negative electrode. A is used as electrode binder. The electrode contains at least one carbon, Si, SiOx or Sn particle or a mixture of some. (4) Heating said electrode at the inert atmosphere to a range of about 50 - 800 °C at a time period of about 1 second to 48 hours, and cool down to ambient temperature to produce electrically conductive polymer binder in the electrode. The heating range can further narrow down to about 150 - 250 °C over a period of about 1 hour. (5) Heating said electrode in at ambient air condition to a range of about 50 - 800 °C at a time period of about 1 second to 48 hours, and cool down to ambient temperature to produce electrically conductive polymer binder in the electrode. The heating range can further narrow down to about 150 - 250 °C over a period of about 1 hour.

[0063] In some embodiments, the heat-treated electrode is used to make a lithium-ion battery.

[0064] It is to be understood that, while the invention has been described in conjunction with the preferred specific embodiments thereof, the foregoing description is intended to illustrate and not limit the scope of the invention. Other aspects, advantages, and modifications within the scope of the invention will be apparent to those skilled in the art to which the invention pertains.

[0065] All patents, patent applications, and publications mentioned herein are hereby incorporated by reference in their entireties.

[0066] The invention having been described, the following examples are offered to illustrate the subject invention by way of illustration, not by way of limitation.

Example 1

From polybutadiene and other dienes to dual-charge conductor polyacetylene

[0067] Synthesis of high free-volume ion and electron transport polyacetylene is shown in Fig. 1. Synthesis of high free-volume ion and electron transport polyphenylene is shown in Fig. 2. Synthesis of high free-volume ion and electron transport polyphenyleneacetylene copolymer is shown in Fig. 3.

[0068] The starting materials are the commercial polybutadiene of molecular weight from 2-butylene at 56 to 1,000,000,000,000 Dalton and could be infinitely high. The brominating of the ally carbon position is done with a general processor, but keep the mole ratio of NBS and the polybutadiene-mer (mer means a repeating unit in a polymer) in a range of 1:1 to 2:1, with 1.1:1 as an particular embodiment.

[0069] NBS bromination at 25° were carried out in purified benzene using AIBN as initiator. All components of the reaction mixture were weighed, dissolved in benzene, and transferred quantitatively to the reaction flask. The reaction medium was degassed three times, sealed from the atmosphere by a stopcock, immersed in a water bath at 25°, and

magnetic stirring for 4 hr. The reaction solution was filtered and precipitated out in methanol and water, and dried at room temperature to yield brominated polybutadiene.

[0070] Hydrolyzation of poly(1-bromobutadiene). poly(1-bromobutadiene) was dissolved in DMF. 1 to 2 mole ratio of the $NaHCO_3$ to the poly(1-bromobutadiene)-mer was added to the DMF solution. While stirring, w1 to 2 mole ratio of water was added dropwise to the stir solution at room temperature to 80 C. After reaction, the solution was filtered and product was precipitated out in hexane solvent. Water dialysis was performed on the product to rid of the salts in the polymer to yield the pure poly(1-hyroxylbutadiene).

[0071] Future heating the pure poly(1-hyroxybutadiene) or in combination with other materials in the inner atmosphere yield a conductive polyacetylene. Depending on the heating temperature, some hydroxyl groups in the poly(1-hyroxybutadiene) can be retained to provide adhesion and other functions.

[0072] The poly(1-hyroxylbutadiene) and other related structures above can be used in fabrication of the electrochemical and other devices to provide both electron and ion dual charge conductivity.

Example 2

Water soluble polyvinyl alcohol (PVA) to dual-charge conductor polyacetylene

[0073] Fig. 6 shows a scheme for converting polyvinyl alcohol into polyacetylene. It shows polyvinyl alcohol full elimination without decomposition. The weight loss is 40.9% of H2O, and weight remaining, 59.1% of polyacetylene. However, the loss of water is always happening with main chain decomposition during thermal treatment even in the inert atmosphere. In order to promote the formation of more polyacetylene structure, and less decomposition during heating process. A base or acid can be added to the polyvinyl alcohol, such as NaOH or H_2SO_4 before heating process. The base and acid added PVA shows lower onset temperature H_2O elimination and prevents from structure decomposition.

[0074] Sample preparation is done in following two ways, as Method 1 and 2.

[0075] Method 1. Make 1% H_2SO_4 by weight water solution. Make 0.5%, 1% or 2% by

weight of NaOH water solution. Add 30 mL of the above solution to 1g of PVA and stirred overnight. Part of the polymer is dissolved and part are swelled in the water solution. The PVA polymer and acid or base solution is concentrated, and all the water is removed in a rotary evaporator at reduced pressure.

[0076] The samples are taken for TGA tests up to 800 °C at variable heating rate under Ar flow.

[0077] Some of the samples go through TGA test to 240 °C at variable heating rate under Ar flow, and cooling to ambient temperature under Ar. These samples are collected after heating, ground into powder and ATR-FTIR spectroscopy tests are performed on the samples.

[0078] Fig. 8 shows PVA thermal decomposition during TGA process in Ar atmosphere. Note: PVA is a pure polymer sample of 130,000 Dalton molecular weight. PVA with 1% weight of 30 mL NaOH solution, PVA:NaOH=10:3 by weight. PVA with 1% weight of 30 mL H_2SO_4 solution, PVA:H_2SO_4=10:3.

[0079] Fig. 7 shows partial elimination of water leaves some –OH functional groups in the structure. Partial elimination of hydroxide group of PVA leads to formation of polyacetylene conductive polymer with functional –OH groups in the polymer structure. These –OH groups can provide additional functions such as adhesion to a surface. The partial elimination can be controlled by thermal decomposition temperature and/or amount of acid or base added.

[0080] For application of converting PVA to polyacetylene, low temperature elimination is preferred. And ideally, the elimination reaction reached a weight loss plateau so the structure is least temperature sensitive and has temperature range to work with. Fig. 9 shows an example of the PVA with 1% NaOH decomposition. The first elimination temperature plateau is 200 °C to 300 °C wide range.

[0081] Fig. 14 shows PVA with 0.5% NaOH solution processed sample. TGA treatment in Ar atmosphere. Note: PVA with 0.5% weight of NaOH solution, PVA:NaOH=20:3 by weight. Theoretical weight retention is 64%.

[0082] Fig. 13 is an example of the PVA with 0.5% NaOH solution processed sample, thermal scan at 6 °C/min heating, stopped at 240 °C TGA treatment in Ar atmosphere. The

sample weight is very close to the theoretical polyacetylene weight based on Scheme 3. The sample collected sample is red colored. Figure 13 shows PVA with 0.5% NaOH water solution treated sample at 12 °C/min heating, stopped at 240 °C TGA treatment in Ar atmosphere. Note: PVA with 0.5% weight of NaOH solution, PVA:NaOH=20:3 by weight. Theoretical weight retention is 64%.

[0083] Method 2. PVA of 5g is mixed with 45g of water and reflux at 100 °C for 1 hour to completely dissolve the PVA in water to form a clear solution. The concentration of the PVA water solution is 10% by weight. 5% weight of PVA water solution also made in the similar way. 1 g of NaOH is dissolved in 9g of water to make a 10% NaOH solution. 0.69g of LiOH is dissolved in 13.29 g of water to make a 5% of LiOH solution.

[0084] PVA 10% solution using 5g of PVA in 45 g of water. NaOH 10% solution using 1g of NaOH in 9g of water. LiOH 5% solution using 0.69g of LiOH in 13.29g of water.

[0085] Examples of different PVA:NaOH ratio of samples are: (1) PVA:NaOH 100:1 by weight was made with mixing 60g of 5% PVA solution and 300 mg of 10% NaOH solution. (2) PVA:NaOH 100:2 by weight was made with mixing 20g of 5% PVA solution and 200 mg of 10% NaOH solution. (3) PVA:NaOH 10:1 by weight was made with mixing 10g of 10% PVA solution and 1g of 10% NaOH solution. (4) PVA:NaOH 10:5 by weight was made with mixing 10g of PVA 10% solution and 5g of 10% NaOH solution. (5) PVA: LiOH 10:0.5 by weight was made mixing with 10g of 10% PVA solution and 1g of 5% LiOH solution. (6) PAV:LiOH 10:2 by weight was made with mixing 10g of 10% PVA solution and 4g of 5% LiOH solution.

[0086] Sample synthesized include PVA 10% solution, no other dopant. PVA and NaOH or LiOH solutions for making polymer film or electrode slurry. 3-5 drops of above polymer and NaOH solutions sample is spread out to a ~2cm by 2cm cover glass. A pure PVA 10% solution is also applied to a cover glass as a control. Three similar samples of each solution were made. All the samples are heated treated dried and process in a tube furnace under flow Ar gas following the heating procedure:

[0087] PVA solution, PVA and LiOH or NaOH solution of different compositions spread on cover glass ready for thermal treatment in tube furnace. Purge for 2.5hrs with Ar gas.

Heating start at 25 °C to 240 °C at liner temperature increase in 3 hrs. Hold at 240 °C for 10 minutes, and cool down to room temperature at ambient temperature.

[0088] Films of the polymer have been synthesized. The samples were all collected as a thin coating on cover glass. The color ranging from light yellow to dark yellow with increase of NaOH content in the film.

[0089] A multimeter is used to measure the lateral/in-plane resistivity/conductivity of the polymer film. The two electrode pins are about 1-2 mm apart on the surface of the polymer film to measure the PAV: LiOH resistivity of the film. Immediate after the films take out of the inert gas tube furnace, none of the samples show measurable film lateral electrical conductivity using the multimeter. The multimeter reading of an infinity resistivity of the lateral film resistivity of all samples.

[0090] However, the polymer films of PVA:NaOH 10:1 and PVA:NaOH 10:5 showed a resistivity reading of 1-50 Mohm of lateral resistivity, corresponding to a significant conductivity of the polymer film after the film expose to ambient air for 15 minutes. The polymer films of PVA:NaOH 100:1 and PVA:NaOH 100:2, after exposed to I_2 vapor for 15 minutes, also showed a resistivity reading of 1-50 Mohm of lateral resistivity, corresponding to a significant conductivity of the polymer film. The pure PVA sample showed infinity resistivity and no conductivity after exposure to air as well as exposure to I_2 vapor.

[0091] Polymer films on cover glass have been synthesized after the thermal treatment process on a sheet of glass. Some samples were exposed to I2 vapor in the glass bottle.

[0092] Polymer film of PVA:NaOH 10:1 on cover glass have been synthesized after the thermal treatment and expose to air for 15 minutes show latera conductivity. The PVA polymer and NaOH solution samples synthesized include: PVA:NaOH 100:2 and PVA:NaOH 10:1.

[0093] 3-4 drops of PVA:NaOH 110:2 and 10:1 are spread out to separate ~2cm by 5cm glass slides. 2 spots of each solution on the slide are made, and 2 slides of the same sample are made. These samples are heated treated dried and process in a tube furnace under ambient air condition following the heating procedure: Tube are open both sides to ambient air.

Heating starts at 25 °C to 240 °C at liner temperature increase in 3 hrs. Hold at 240 °C for 10 minutes, and cool down to room temperature at ambient temperature.

[0094] The polymer films show infinite resistivity based on the lateral multimeter measurement. However, when the 10:1 sample treated in I_2 for 15 minutes, and the 100:2 sample treated overnight, the film shows 1-50 Mohm resistivity.

Example 3

Electrode slurry, and electrode preparation

[0095] PVA:NaOH 10:1 by weight was made with mixing 10g of 10% PVA solution and 1g of 10% NaOH solution. This composition is used to make 2:8 ratio of PVA and Si electrode slurry, containing NaOH. 1 g of Si micronsize particle (1-5 μm diameter) is mixed with 2.75 g of the PVA:NaOH 10:1 mixture in a small agate mortar, and mixed with a agate pestle for 10 minutes to form a homogenous slurry.

[0096] The slurry was coated on a thin Cu sheet using a doctor blade with a 50 μm gap at a 2 meter/min rate. The electrode was dried in air for ~1 hour. The PVA and Si electrode slurry is coated onto an electrode laminate on a Cu current collector.

[0097] One piece of the electrode is dried at 80 ℃ under vacuum overnight. This electrode is named SiPN80. The Si loading of the electrode is 1.1 mg/cm^2.

[0098] The other piece of the electrode was processed in a tube furnace follow the procedure. The it is purged for 2.5hrs with Ar gas. Heating started at 25 °C to 240 °C with liner temperature increase in 3 hrs. Hold at 240 °C for 10 minutes, and cooled down to room temperature at ambient temperature. This electrode is named SiPN240. The Si loading of the electrode is 1.1 mg/cm^2.

[0099] The other piece of the electrode was processed in a tube furnace follow the procedure. Heating start at 25 °C to 240 °C with liner temperature increase in 3 hrs in air. Hold at 240 °C for 10 minutes, and cool down to room temperature at ambient temperature. This electrode is named SiPNA240.

[00100] The other piece of the electrode was processed in a tube furnace follow the procedure. Heating start at 25 °C to 150 °C with liner temperature increase in 1 hr in air. Hold at 240 °C for 10 minutes, and cool down to room temperature at ambient temperature. This electrode is named SiPNA150. PVA and Si electrode with or without NaOH doping are thermal treat in a tube furnace.

[00101] The PVA was synthesized using a 10% water solution. This composition is used to make 2:8 ratio of PVA and Si electrode slurry. 1 g of Si micron-sized particle (1-5 μm diameter) is mixed with 2.0 g of the PVA 10% water solution in a small agate mortar, and mixed with an agate pestle for 10 minutes to form a homogenous slurry.

[00102] The slurry was coated on a thin Cu sheet using a doctor blade with a 50 μm gap at a 2 meter/min rate. The electrode was dried in air for ~1 hour. One piece of the electrode is dried at 80 °C under vacuum overnight. This electrode is named SiP80.

[00103] Another piece of the electrode was processed in a tube furnace follow the procedure. Purge for 2.5hrs with Ar gas. Heating start at 25 °C to 240 °C with liner temperature increase in 3 hrs. Hold at 240 °C for 10 minutes, and cool down to room temperature at ambient temperature. This electrode is named SiP240.

[00104] PVA:NaOH 100:2 by weight was made with mixing 10g of 5% PVA solution and 0.1 g of 10% NaOH solution. This composition is used to make 2:8 ratio of PVA and Si electrode slurry, containing NaOH. 1 g of Si micronsize particle (1-5 μm diameter) is mixed with 5.10 g of the PVA:NaOH 100:2 mixture in a small agate mortar, and mixed with an agate pestle for 10 minutes to form a homogenous slurry.

[00105] The slurry was coated on a thin Cu sheet using a doctor blade with a 50 μm gap at a 2 meter/min rate. The electrode was dried in air for ~1 hour. Electrode name: SiPN02. The Si electrode was made with a PVA:NaOH 100:2 mixture.

Example 4

Generic description of the class polymer structures that can be processed to dual-charge (ion and electron) conductors

[00106] The poly(1-hyroxylbutadiene) and PVA (Scheme 1,2,3) with NaOH can be used as electrode binders for carbon, Si, Sn and other alloy based composite electrodes. This class of functional conductive polymer materials provides strong adhesion to the Si, Sn and carbon materials and Cu current collectors as an effective electrode binder. Thermal treatment of the polymer materials leads to all or partial loss of the hydroxyl groups to provide permanent and superb pathways ranging from Angstroms to Nanometers in the polymer films for lithium ion transport. When the polymers are applied on surface of Si or graphite, the polymers in touch with the active materials (Si, Sn and Carbon) surface transforms into passivation layer during the electrochemical process to provide very strong passivation to the active materials surface. The ion pathway in the polymer binder due to the thermal decomposition of hydroxyl groups provides ion transport. Unlike the usage of only a few percent of conventional binders, it is preferentially to use this functional binder to cover the entire active materials particles surface to provide both strong adhesion and surface protection. We also anticipate this class of electrode binders works for the anode for Na and K based battery, and for solid-state batteries.

Example 5

Cell fabrication and testing

[00107] Coin cells (2032, Hohsen Co.) were assembled in an argon-filled glovebox. A 14.42 mm diameter disk was punched out as a working electrode. Lithium chip (16.0 mm in diameter, MTI Co.), is used as the counter electrodes in half. 60 μL of lithium-ion electrolyte of 1M $LiPF_6$ in EC:EMC (3:7 by weight) and fluoroethylene carbonate (FEC, typically 5 wt.%) is used for coin cell testing. The Si loading of the electrode is ~1.0 mg/cm^2. Celgard 2400 separator (1.7 cm in diameter) was placed between the working electrode and the counter electrode.

[00108] The galvanostatic cycling performance of the assembled coin cells was evaluated with Maccor Cycler in a thermal chamber at 30 °C. The C-rate was determined based on the theoretical capacity upon a full lithiation of Si materials of 4200 mAh/g. The Cell is rested for 4 hours and lithiated at C/25 current rate.

[00109] Fig. 20. (A) The electrode of SiPN240 can be lithiated to almost full capacity. This

electrode is made with PVA:NaOH 10:1 water solution with Si. (B) The electrode of SiP240 cannot be lithiated. This electrode is made with PVA 10% water solution with Si.

[00110] PVA NaOH films are made from solution on cover glass. The PVA:NaOH films undergo heat treatment in a tube furnace of under Ar.

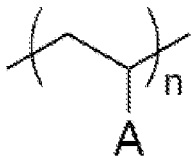
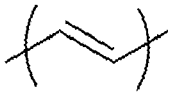
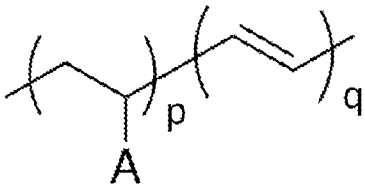
[00111] PVA:NaOH and PVA:LiOH combinations are synthesized under water solutions. The PVA:NaOH and PVA:LiOH solution are cast droplet on cover glass, which then undergo heat treatment on the cover glass under Ar. The PVA:NaOH casted films after heat treatment showed lateral electrical conductivity. The PVA:NaOH casted films under open air heat treatment.

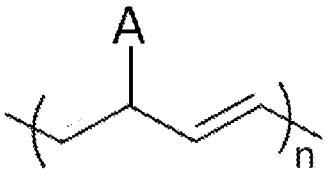
[00112] PVA:NaOH and Si particles are used to make an electrode slurry. The PVA:NaOH and Si are cast to make a PVA:NaOH and Si electrode. The PVA:NaOH and Si electrode is air dried. The PVA:NaOH and Si electrode can be cut. The PVA:NaOH and Si electrode can undergo heat treatment, such as in a tube furnace.

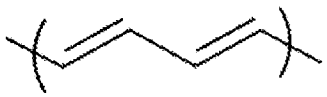
[00113] While the present invention has been described with reference to the specific embodiments thereof, it should be understood by those skilled in the art that various changes may be made and equivalents may be substituted without departing from the true spirit and scope of the invention. In addition, many modifications may be made to adapt a particular situation, material, composition of matter, process, process step or steps, to the objective, spirit and scope of the present invention. All such modifications are intended to be within the scope of the claims appended hereto.

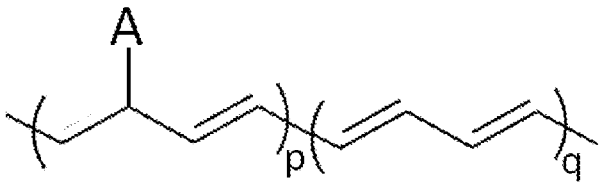
[00114] All cited references are hereby each specifically incorporated by reference in their entireties.

WHAT IS CLAIMED IS:

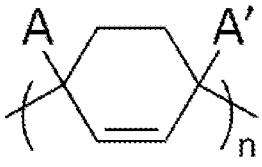
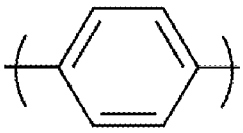
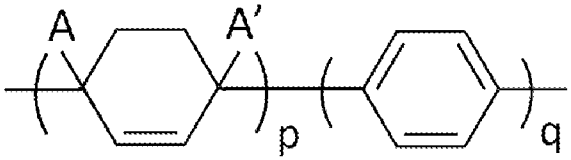
1. A method of forming a conductive polymer, comprising (a) providing a polyvinyl polymer having the following chemical structure:  (I-a), wherein A is –OH, –OR, F, Cl, Br, I, $–SO_4R$, $–SO_3R$, $–NH_2$, $–NH_R$, $–NR_1R_2$, a phenyl, or a phenyl derivative, and R, R_1, and/or R_2 are each independently an organic substituent; and (b) heating the polyvinyl polymer thereby forming at least one  to form the following chemical structure:  (I-b), wherein p has a value of $0 \leq p < 1$, q has a value of $0 < q \leq 1$, and $p + q = 1$.
2. The method of claim 1, wherein p has a value of $0 \leq p \leq 0.9$ and q has a value of $0.1 \leq q \leq 1$.
3. The method of claim 2, wherein p has a value of $0 \leq p \leq 0.8$ and q has a value of $0.2 \leq q \leq 1$.
4. The method of claim 3, wherein p has a value of $0 \leq p \leq 0.7$ and q has a value of $0.3 \leq q \leq 1$.
5. The method of claim 4, wherein p has a value of $0 \leq p \leq 0.6$ and q has a value of $0.4 \leq q \leq 1$.
6. The method of claim 5, wherein p has a value of $0 \leq p \leq 0.5$ and q has a value of $0.5 \leq q \leq 1$.
7. The method of claim 6, wherein p has a value of $0 \leq p \leq 0.4$ and q has a value of $0.6 \leq q \leq 1$.
8. The method of claim 7, wherein p has a value of $0 \leq p \leq 0.3$ and q has a value of $0.7 \leq q \leq 1$.
9. The method of claim 8, wherein p has a value of $0 \leq p \leq 0.2$ and q has a value of $0.8 \leq q \leq 1$.

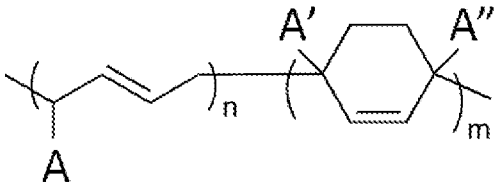
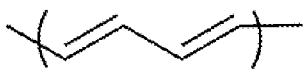
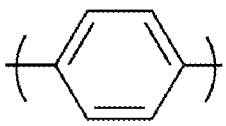
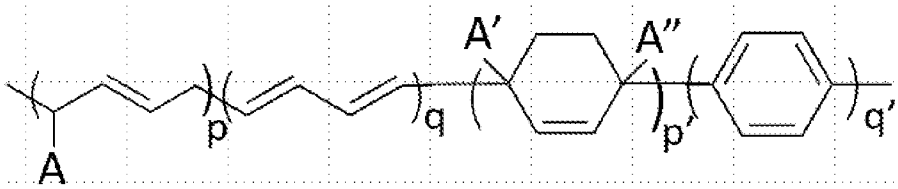
10. The method of claim 9, wherein p has a value of $0 \leq p \leq 0.1$ and q has a value of $0.9 \leq q \leq 1$.
11. The method of claim 10, wherein p is 0 and q is 1.
12. The method of claim 1, further comprising adding an acid or base to the polyvinyl polymer to form a mixture is prior to the heating step (b).
13. The method of claim 12, wherein the acid or base added to the polyvinyl polymer is 0.0001% to 99.9% by weight of the mixture.
14. The method of claim 12, comprising adding an acid to the polyvinyl polymer to form a mixture prior to the heating step (b), wherein the acid is H_2SO_4, H_3PO_4, HNO_3, HCl, HBr, HI, HPF_6, HTFSI. HFSI, $NClO_4$, $HBrO_4$, HIO_4, or a mixture thereof.
15. The method of claim 12, comprising adding a base to the polyvinyl polymer to form a mixture prior to the heating step (b), wherein the base is LiOH, NaOH, KOH, RbOH, CsOH, $Mg(OH)_2$, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$, or a mixture thereof.
16. The method of claim 1, wherein the chemical structure (I-b) is in a thin film.
17. The method of claim 1, comprising passing an electric current through chemical structure (I-b).
18. A method of forming a conductive polymer, comprising (a) providing a precursor polymer having the following chemical structure: 

(II-a), wherein A is –OH, –OR, F, Cl, Br, I, $–SO_4R$, $–SO_3R$, $–NH_2$, $–NH_R$, $–NR_1R_2$, a phenyl, or a phenyl derivative, and R, R_1, and/or R_2 are each independently an organic substituent; and (b) heating the precursor polymer thereby forming at least one  to form the following chemical structure:



(II-b), wherein p has a value of $0 \leq p < 1$, q has a value of $0 < q \leq 1$, and $p + q = 1$.

19. A method of forming a conductive polymer, comprising (a) providing a precursor polymer having the following chemical structure:  (III-a), wherein A and A' are each independently –OH, –OR, F, Cl, Br, I, $–SO_4R$, $–SO_3R$, $–NH_2$, $–NH_R$, $–NR_1R_2$, a phenyl, or a phenyl derivative, and R, R_1, and/or R_2 are each independently an organic substituent; and (b) heating the precursor polymer thereby forming at least one  to form the following chemical structure:  (III-b), wherein p has a value of $0 \leq p < 1$, q has a value of $0 < q \leq 1$, and $p + q = 1$.

20. A method of forming a conductive polymer, comprising (a) providing a precursor polymer having the following chemical structure:  (IV-a), wherein A, A', and A" are each independently –OH, –OR, F, Cl, Br, I, $–SO_4R$, $–SO_3R$, $–NH_2$, $–NH_R$, $–NR_1R_2$, a phenyl, or a phenyl derivative, and R, R_1, and/or R_2 are each independently an organic substituent, n has a value of $0 < n < 1$, m has a value of $0 < m < 1$, and $n + m = 1$; and (b) heating the precursor polymer thereby forming at least one  and at least one  to form the following chemical structure:  (IV-b), wherein

p has a value of $0 \leq p < n$, q has a value of $0 < q \leq n$, p' has a value of $0 \leq p' < m$, q' has a value of $0 < q' \leq m$, $p + q = n$, $p' + q' = m$, and $p + q + p' + q' = 1$.

21. The method of claims 1-20, further comprising doping the polymer having the chemical structure of (I-b), (II-b), (III-b), or (IV-b) with O_2, I_2, PF_6^-, or like anion, and/or metal cation, to further enhance electronic conductivity.
22. An electrically conductive composition comprising one or more polymers, wherein each polymer has the chemical structure of (I-b), (II-b), (III-b), (IV-b), or a mixture thereof.
23. An electric device comprising an electric circuit comprising the composition comprising the one or more polymers having a chemical structure of (I-b), (II-b), (III-b), (IV-b), or a mixture thereof, wherein an electric current is pass through the chemical structure of (I-b), (II-b), (III-b), (IV-b), or a mixture thereof.
24. The electric device of claim 23, wherein the one or more polymers are electrode binders with electrode materials.

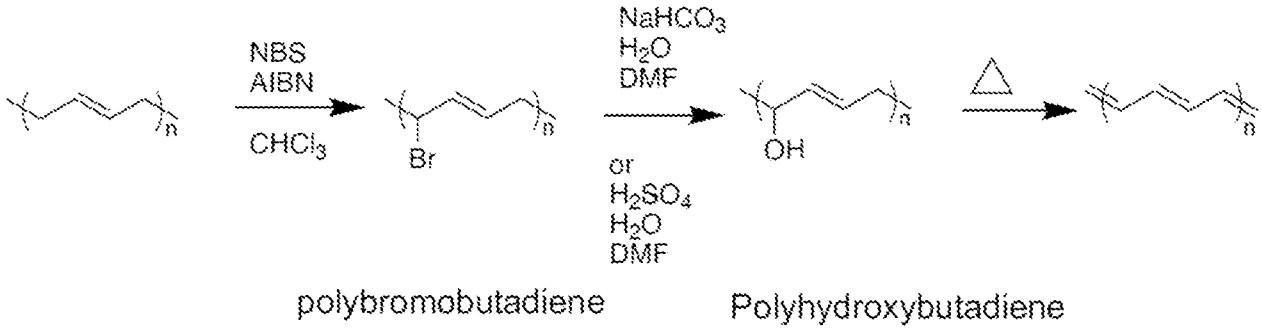


FIG. 1

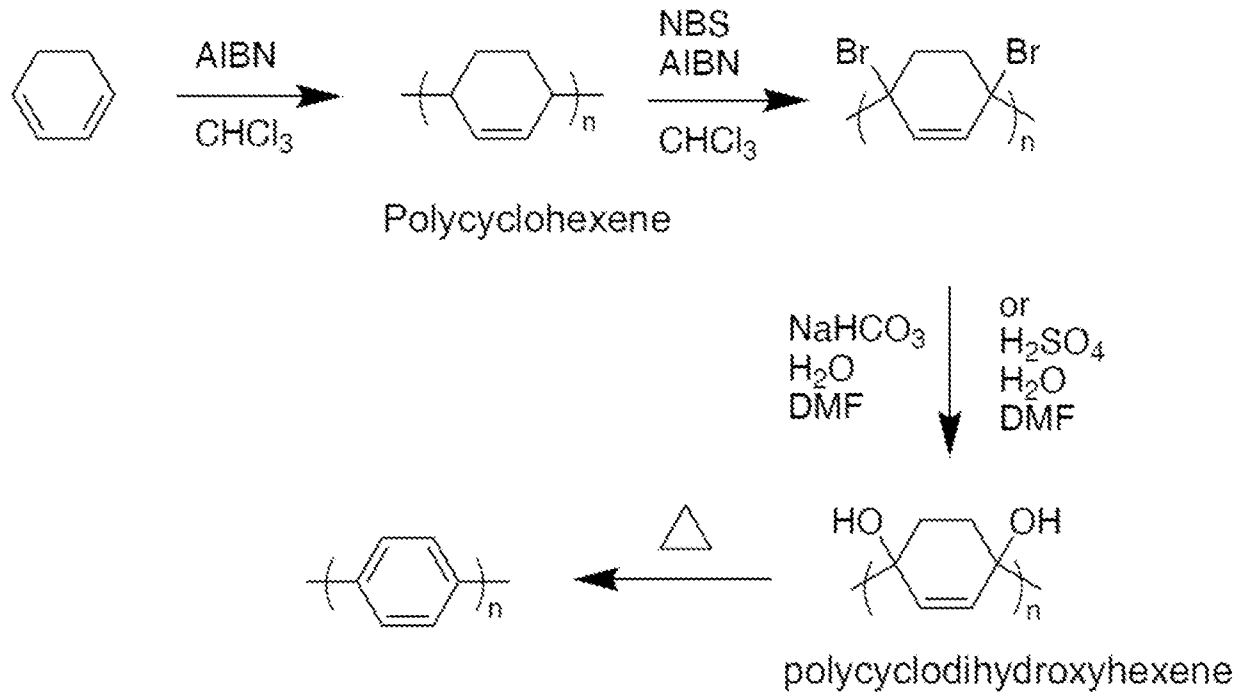


FIG. 2

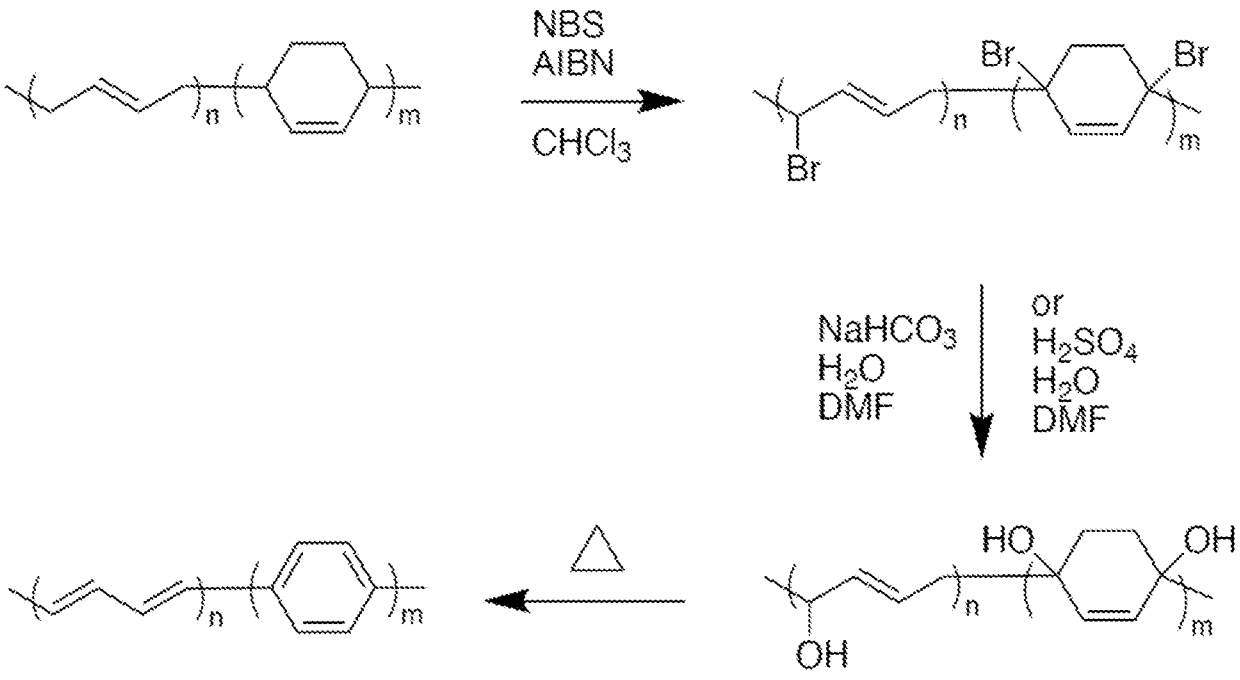
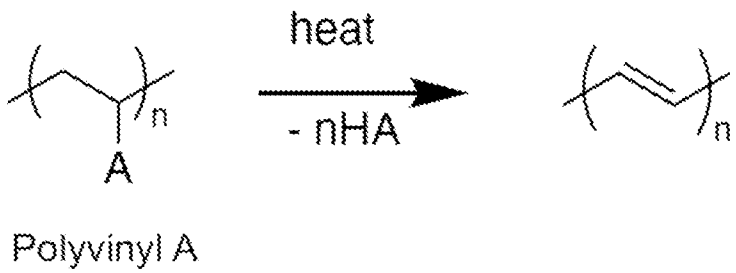
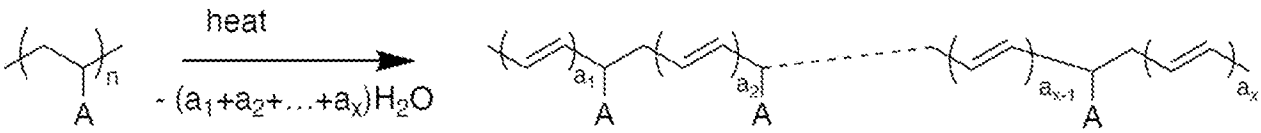


FIG. 3



Polyvinyl A

FIG. 4



Polyvinyl A

FIG. 5

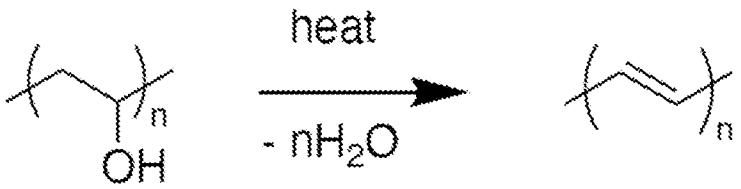


FIG. 6

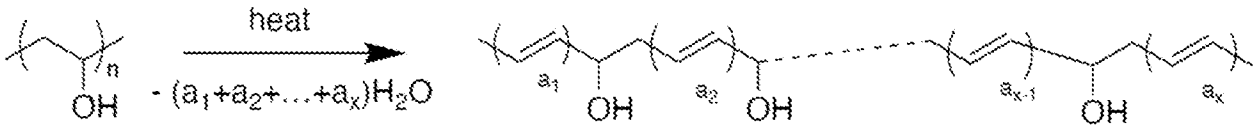


FIG. 7

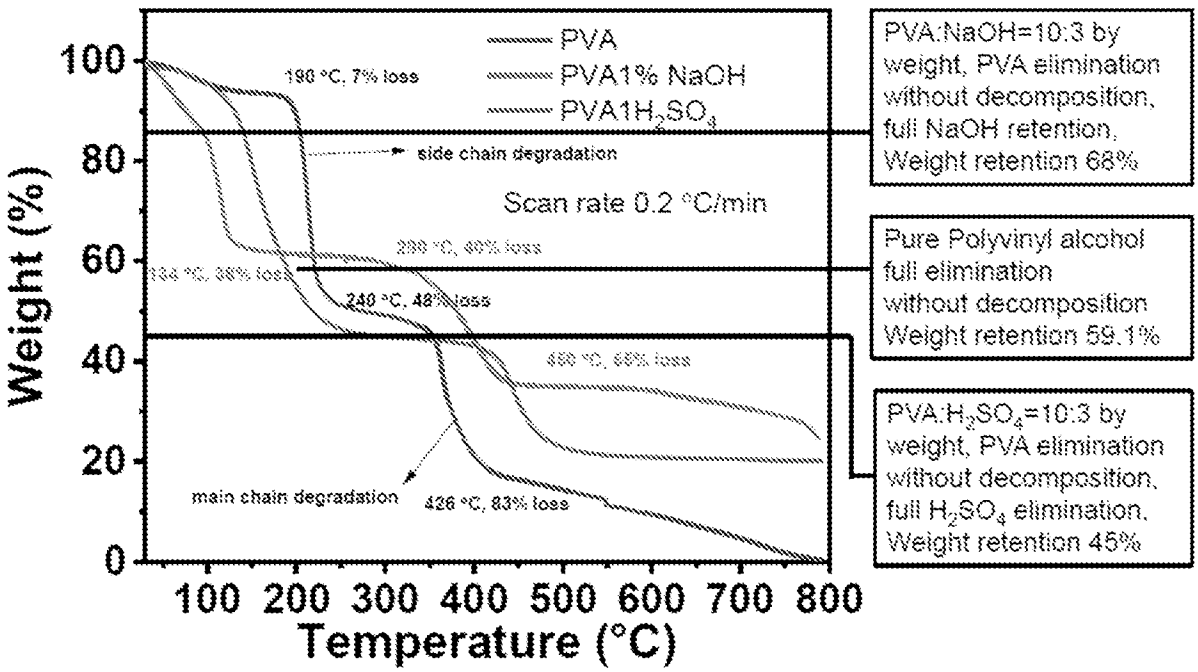

PVA
PVA1% NaOH
PVA1H2SO4
196 °C, 7% loss
side chain degradation
Scan rate 0.2 °C/min
280 °C, 40% loss
134 °C, 8% loss
240 °C, 48% loss
460 °C, 65% loss
main chain degradation
426 °C, 83% loss
Weight (%)
Temperature (°C)
PVA:NaOH=10:3 by weight, PVA elimination without decomposition, full NaOH retention, Weight retention 68%
Pure Polyvinyl alcohol full elimination without decomposition Weight retention 59.1%
PVA:H2SO4=10:3 by weight, PVA elimination without decomposition, full H2SO4 elimination, Weight retention 45%

FIG. 8

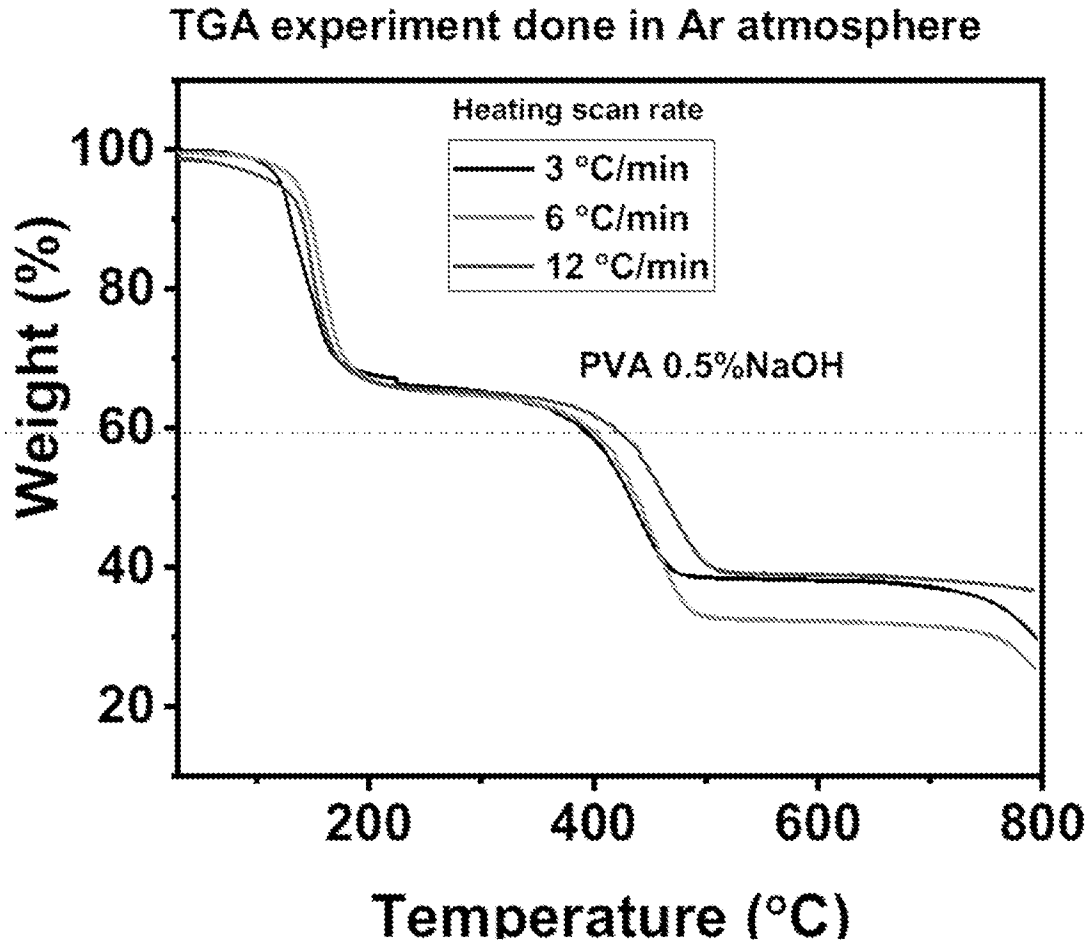

TGA experiment done in Ar atmosphere
Heating scan rate
3 °C/min
6 °C/min
12 °C/min
PVA 0.5%NaOH
Weight (%)
Temperature (°C)

FIG. 9

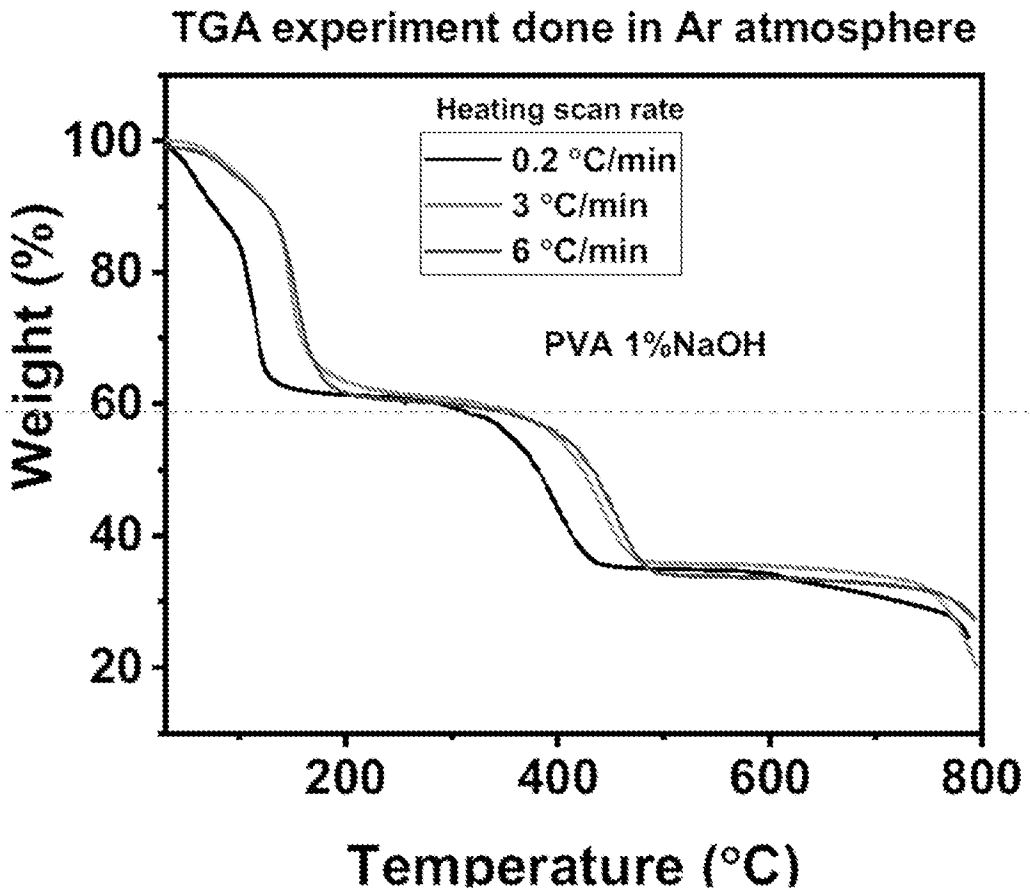

TGA experiment done in Ar atmosphere
Heating scan rate
0.2 °C/min
3 °C/min
6 °C/min
PVA 1%NaOH
Weight (%)
100
80
60
40
20
200
400
600
800
Temperature (°C)

FIG. 10

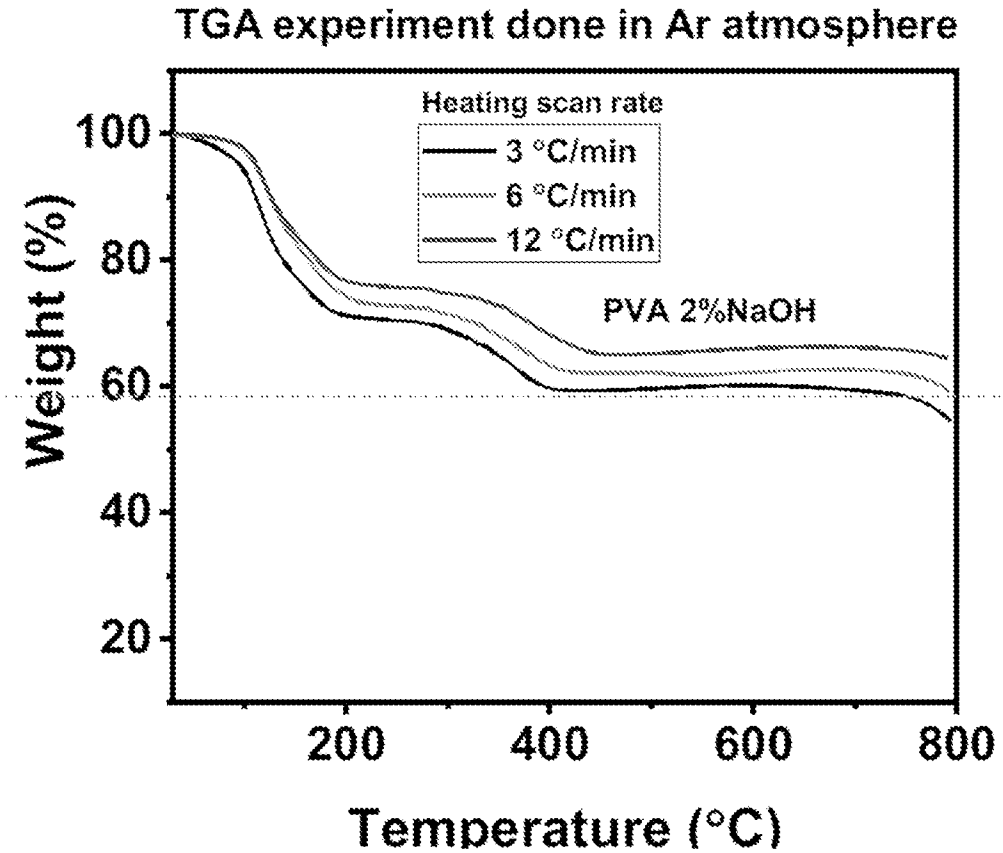

TGA experiment done in Ar atmosphere
Heating scan rate
3 °C/min
6 °C/min
12 °C/min
PVA 2%NaOH
Weight (%)
100
80
60
40
20
200
400
600
800
Temperature (°C)

FIG. 11

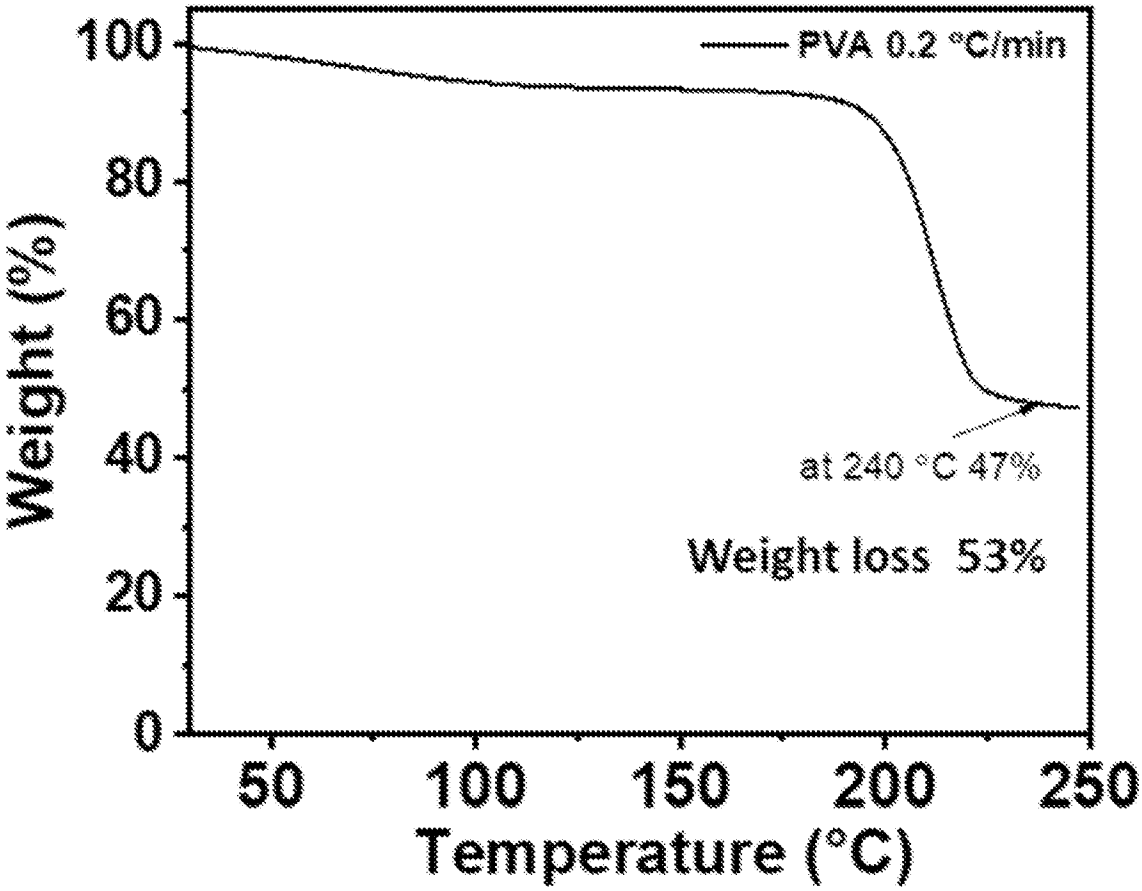

PVA 0.2 °C/min
at 240 °C 47%
Weight loss 53%
Weight (%)
Temperature (°C)
0
20
40
60
80
100
50
100
150
200
250

FIG. 12

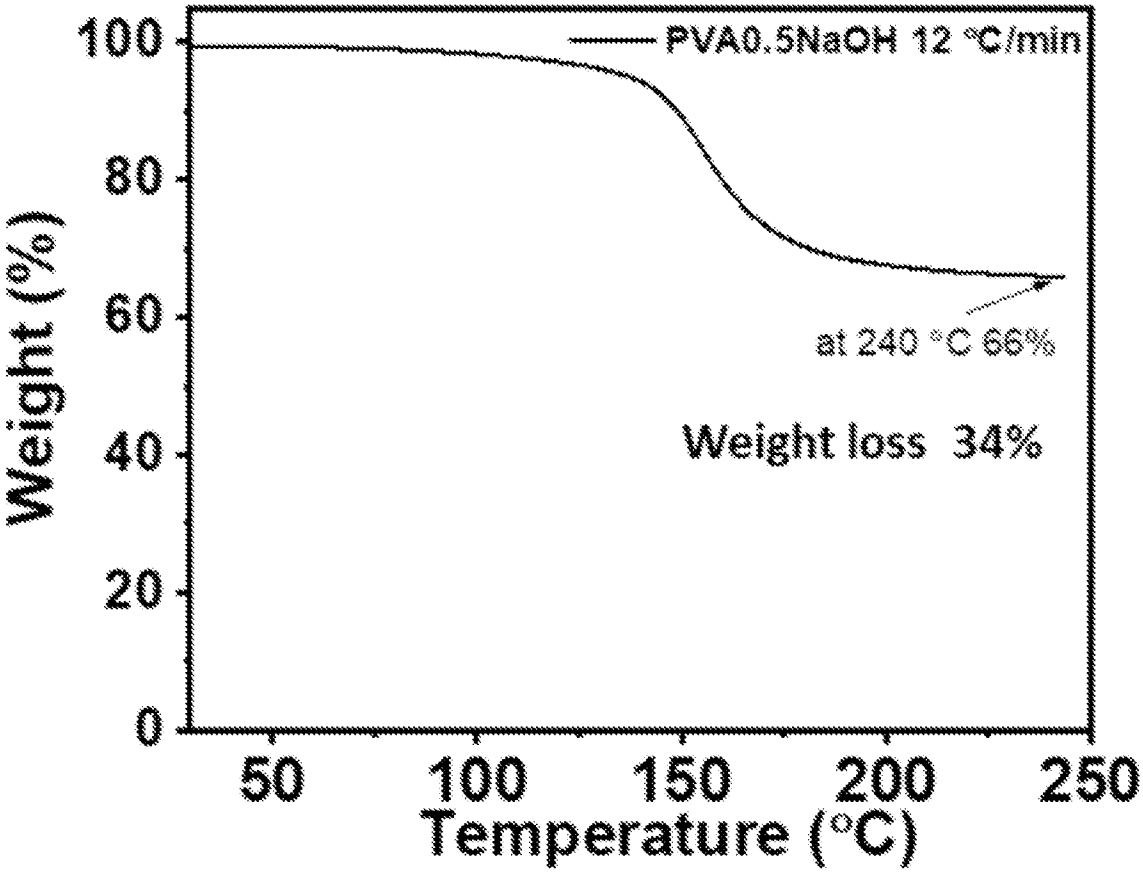

PVA0.5NaOH 12 °C/min
at 240 °C 66%
Weight loss 34%
Weight (%)
Temperature (°C)
0
20
40
60
80
100
50
100
150
200
250

FIG. 13

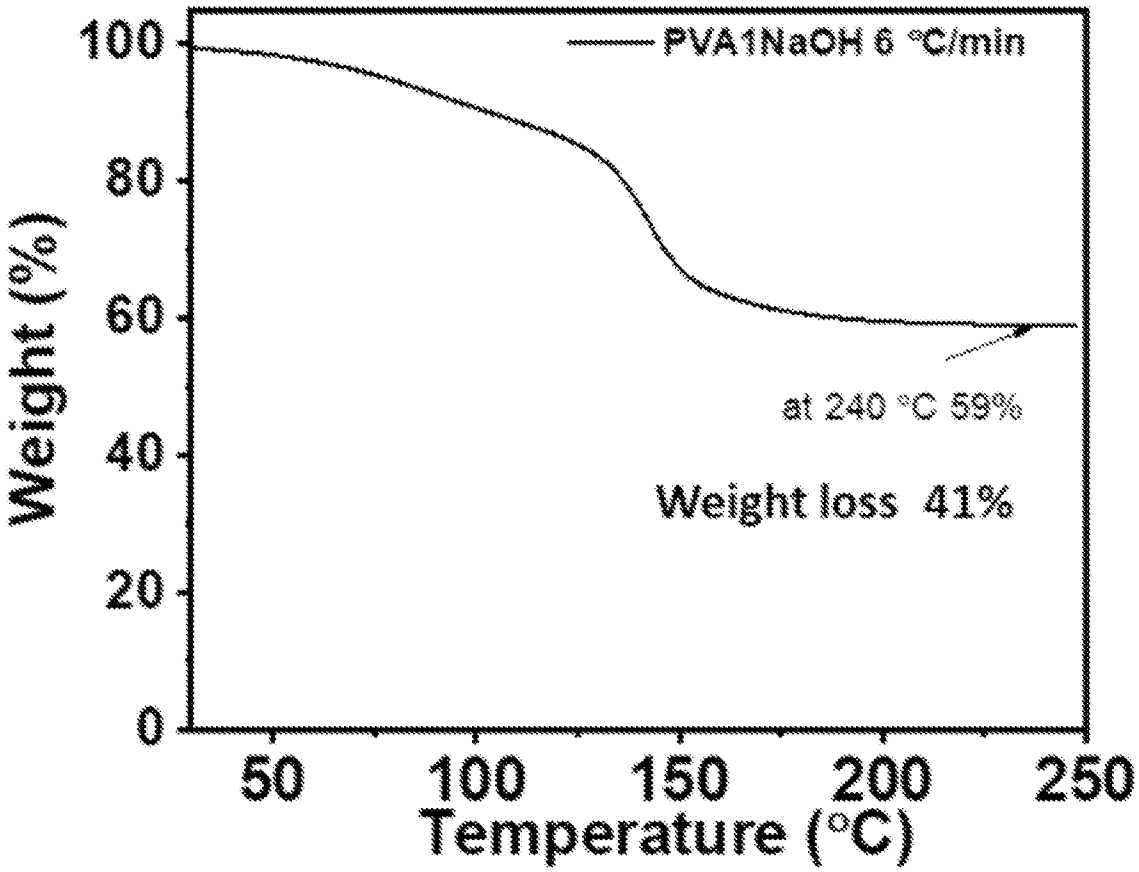

PVA1NaOH 6 °C/min
at 240 °C 59%
Weight loss 41%
Weight (%)
Temperature (°C)
100
80
60
40
20
0
50
100
150
200
250

FIG. 14

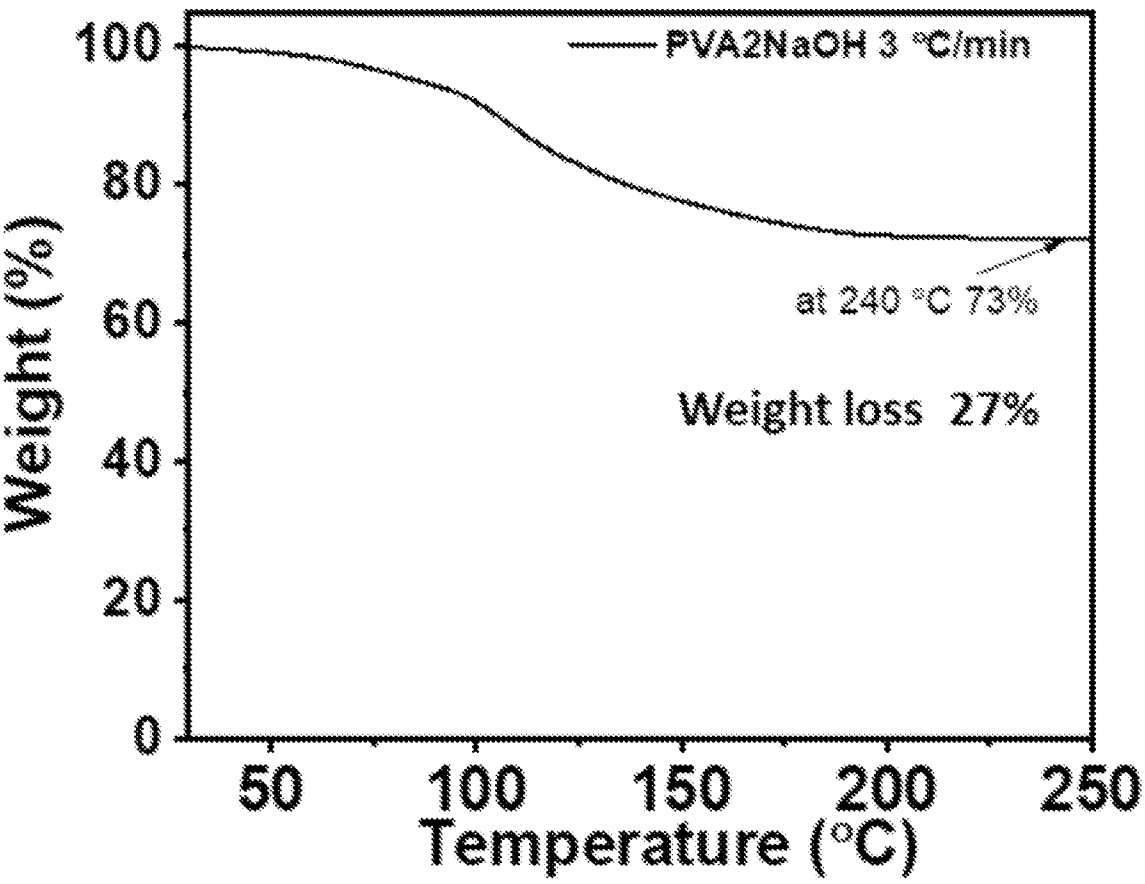

PVA2NaOH 3 °C/min
at 240 °C 73%
Weight loss 27%
Weight (%)
Temperature (°C)
100
80
60
40
20
0
50
100
150
200
250

FIG. 15

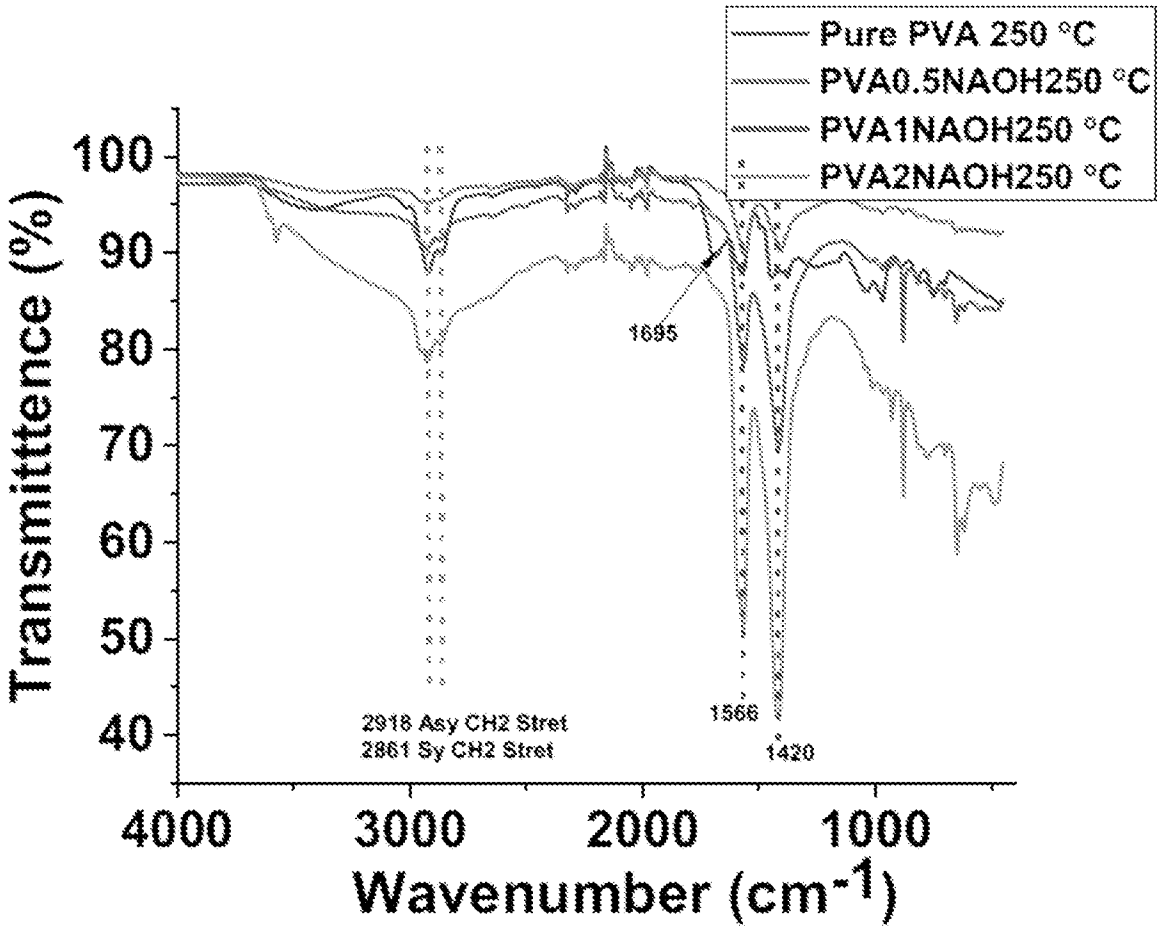

Pure PVA 250 °C
PVA0.5NAOH250 °C
PVA1NAOH250 °C
PVA2NAOH250 °C
Transmittence (%)
100
90
80
70
60
50
40
1695
1566
1420
2918 Asy CH2 Stret
2861 Sy CH2 Stret
4000
3000
2000
1000
Wavenumber (cm-1)

FIG. 16

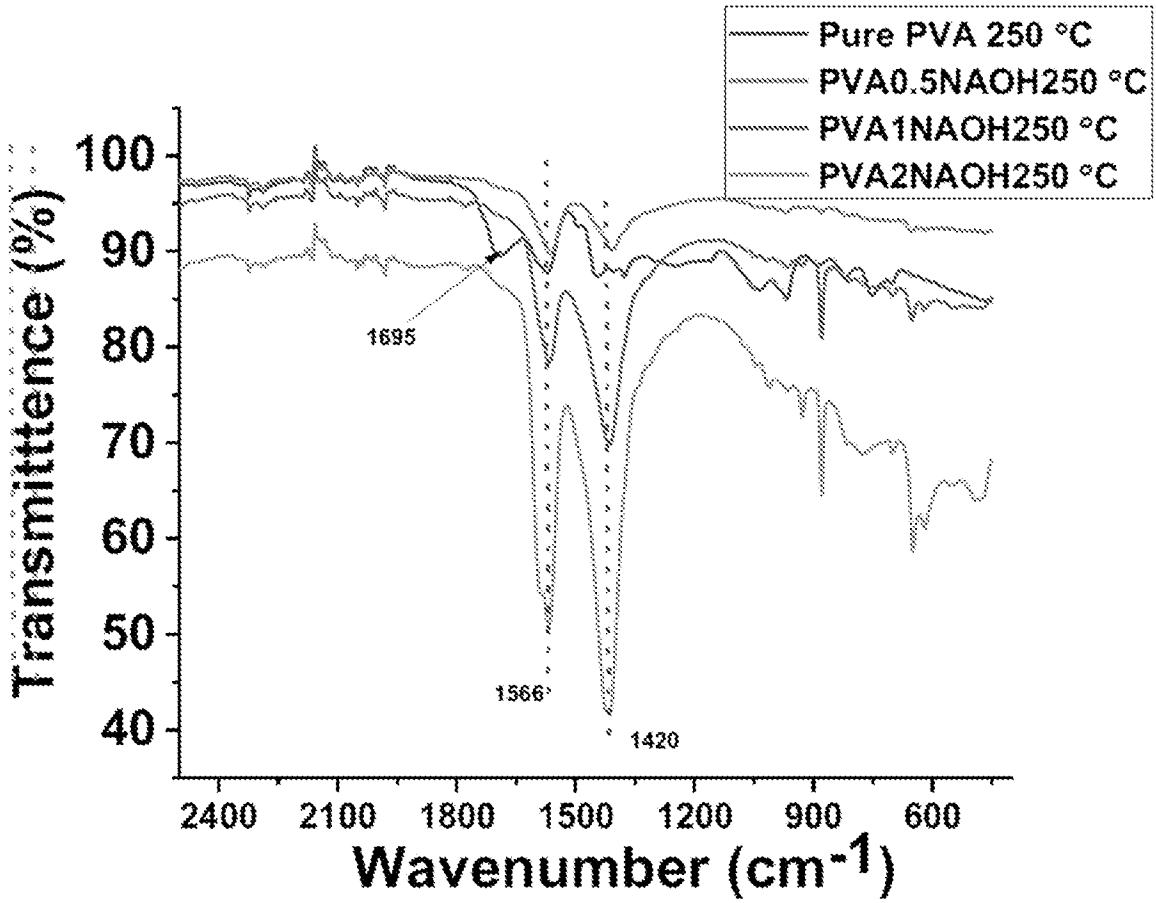

Pure PVA 250 °C
PVA0.5NAOH250 °C
PVA1NAOH250 °C
PVA2NAOH250 °C
Transmittence (%)
100
90
80
70
60
50
40
1695
1566
1420
2400
2100
1800
1500
1200
900
600
Wavenumber (cm-1)

FIG. 17

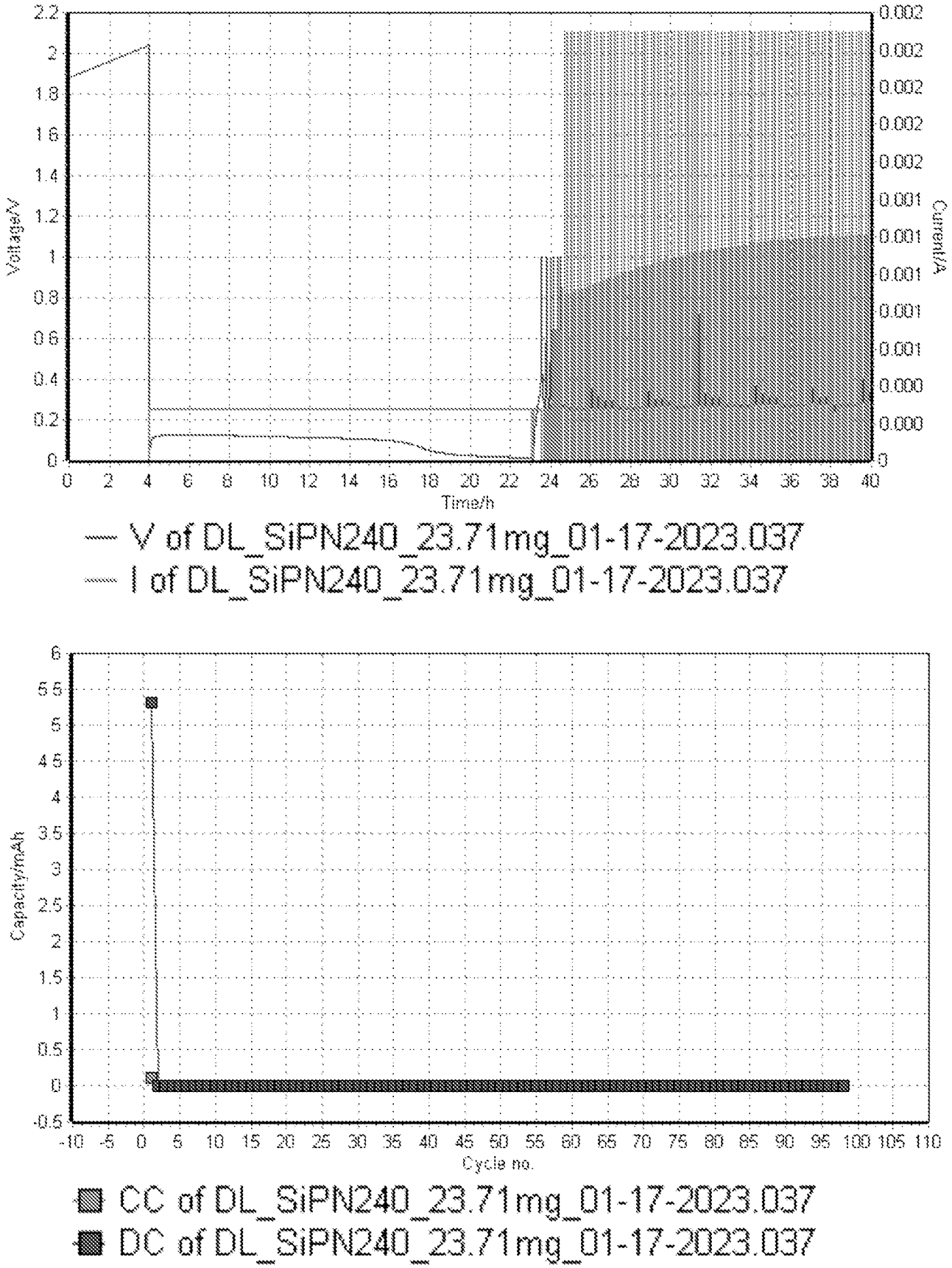

Voltage/V
Current/A
Time/h
V of DL_SiPN240_23.71mg_01-17-2023.037
I of DL_SiPN240_23.71mg_01-17-2023.037
Capacity/mAh
Cycle no.
CC of DL_SiPN240_23.71mg_01-17-2023.037
DC of DL_SiPN240_23.71mg_01-17-2023.037

FIG. 18

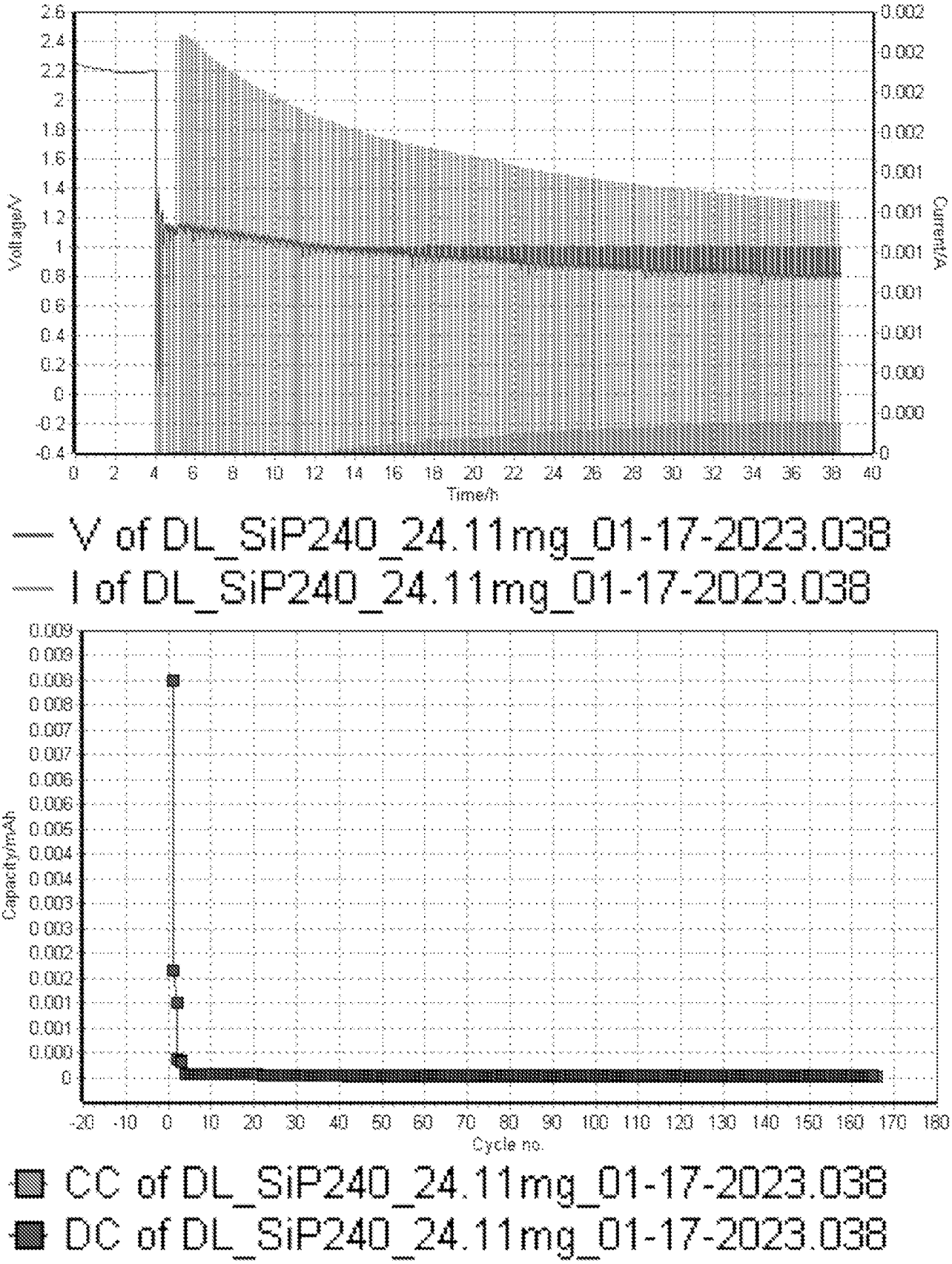

Voltage/V
Current/A
Time/h
V of DL_SiP240_24.11mg_01-17-2023.038
I of DL_SiP240_24.11mg_01-17-2023.038
Capacity/mAh
Cycle no.
CC of DL_SiP240_24.11mg_01-17-2023.038
DC of DL_SiP240_24.11mg_01-17-2023.038

FIG. 19

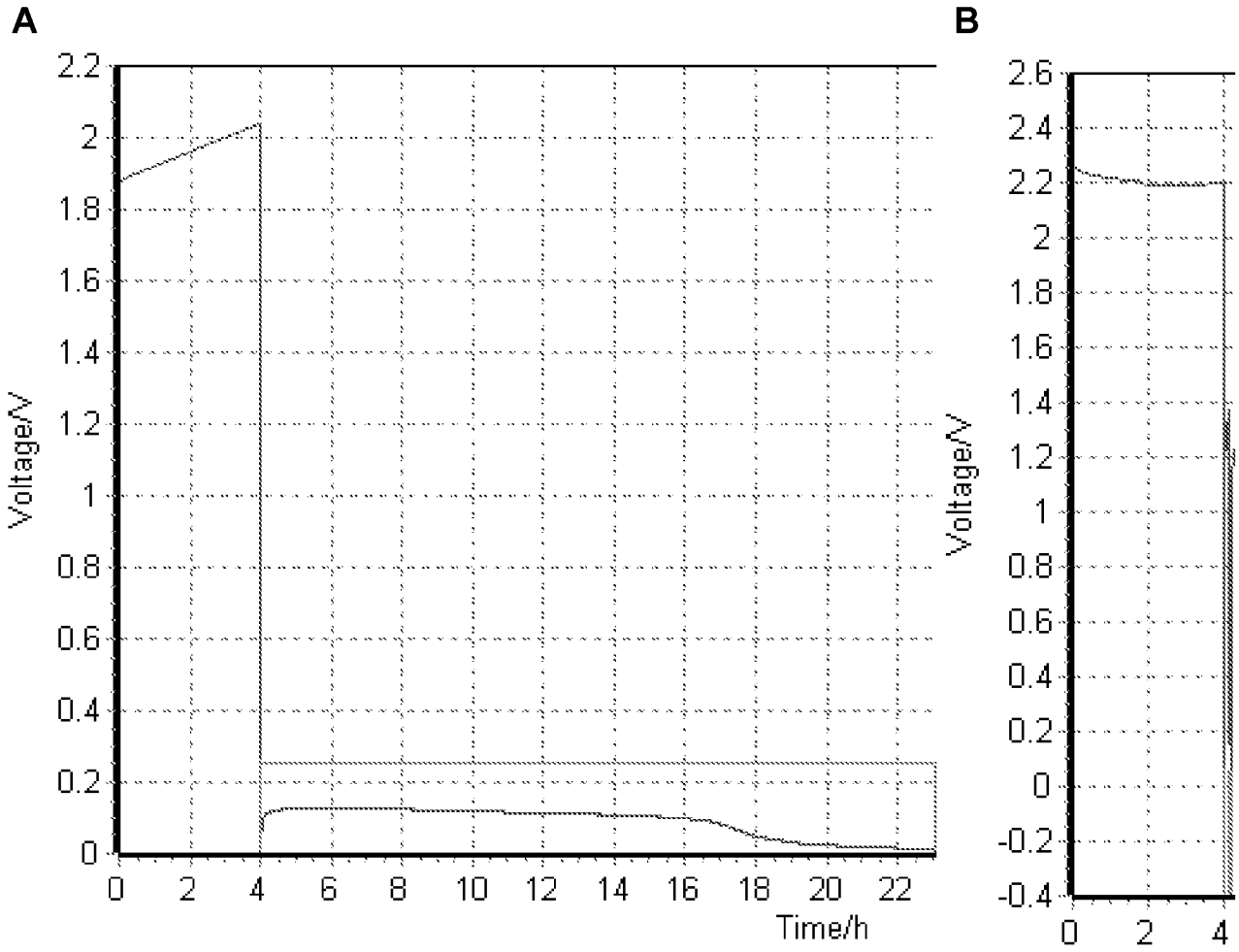

A
B
Voltage/V
Time/h
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0 2 4 6 8 10 12 14 16 18 20 22
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
0 2 4

FIG. 20