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(54) **Title:** METHOD FOR PROCESSING CONDUCTIVE POLYMER BINDER FOR ELECTROCHEMICAL DEVICES

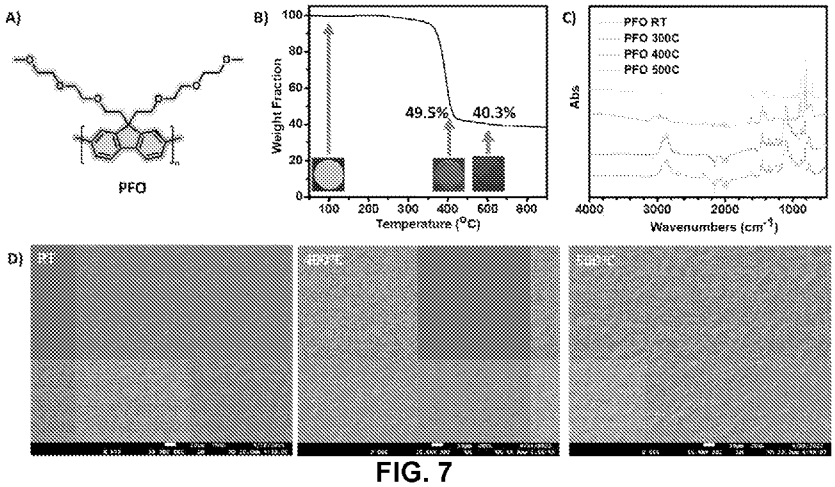

FIG. 7

(57) **Abstract:** The present invention provides for a method for applying an electrically conductive polymer to a surface, comprising: (a) providing an electrically conductive polymer that is soluble in an alcohol-water solvent or water; (b) introducing an alcohol to the polymer to form a solution; (c) introducing water to the solution; (d) adding a conductive material to the solution to produce a slurry; (e) applying the slurry to a surface; (f) drying the slurry applied to the surface to evaporate part or all of the alcohol and water; and (g) heating or thermally treating the binder to a temperature that decomposes or removes part or all side chains of the electrically conductive polymer.

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[Continued on next page]

Published:
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Method for processing conductive polymer binder for electrochemical devices

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the priority benefit of U.S. Provisional Application Nos. 63/614,257, filed December 22, 2023, which is hereby incorporated by reference in its entirety.

STATEMENT OF GOVERNMENTAL SUPPORT

[0002] The invention was made with government support under Contract Nos. DE-AC02-05CH11231 awarded by the U.S. Department of Energy. The government has certain rights in the invention.

FIELD OF THE INVENTION

[0003] The present invention is in the field of conductive polymer binders.

BACKGROUND OF THE INVENTION

[0004] Rechargeable lithium-ion batteries hold great promise as energy storage devices to solve the temporal and geographical mismatch between the supply and demand of electricity, and are therefore critical for many applications such as portable electronics and electric vehicles. Electrodes in these batteries are based on intercalation reactions in which Li+ ions are inserted (extracted) from an open host structure with electron injection (removal). There is a need for a low cost and environmental benign method for synthesizing electrically conductive polymer binders.

[0005] In recent years, lithium-ion batteries have been widely used in electric vehicles and electronics. Among most commercial lithium-ion batteries, graphite is used as an anode material because of its ability to ensure high voltage coupled with lithium-ion cathode and high capacity. Spent lithium-ion battery anode is difficult to recycle and revitalize, because the pyrometallurgy and hydrometallurgy processes only work well with metals oxide cathode. In addition, even if the spent graphite were recovered, it could not be directly applied for new electrode fabrication due to its poor interface conductivity and mechanical disintegration.

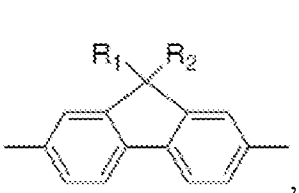
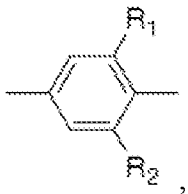
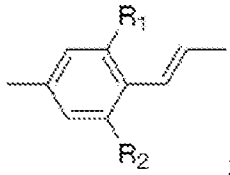
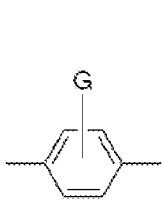
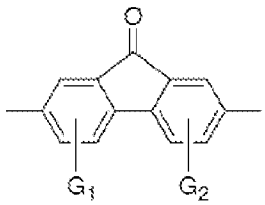
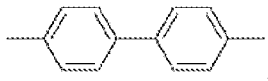
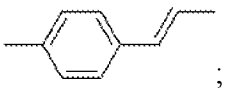
SUMMARY OF THE INVENTION

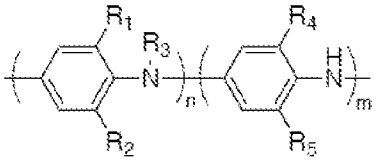
[0006] The present invention provides for a method for applying an electrically conductive polymer to a surface, comprising: (a) providing an electrically conductive polymer that is soluble in an alcohol-water solvent or water; (b) introducing an alcohol to the polymer to form a solution; (c) introducing water to the solution; (d) adding a conductive material to the solution to produce a slurry; (e) applying the slurry to a surface; (f) drying the slurry applied to the surface to evaporate part or all of the alcohol and water; and (g) heating or thermally treating the binder to a temperature that decomposes or removes part or all side chains of the electrically conductive polymer.

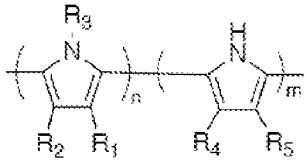
[0007] The electrically conductive polymer or conductive polymer that has been heated or thermally treated by the method of the present invention undergoes thermal pyrolysis and the electrically conductive polymer or conductive polymer is converted into a "final form", or having a "hierarchically ordered structure (HOS)". The electrically conductive polymer or conductive polymer is converted into an electrically conductive polymer in a final form, or a conductive polymer in a final form, or a HOS- electrically conductive polymer or HOS-conductive polymer. In some embodiments, the conductive polymer is a poly(9,9-dioctylfluorene-*co*-fluorenone-*co*-methylbenzoic ester) (PFM), and a PFM heated or thermally treated by the method of the present invention is a HOS-PFM. When the electrically conductive polymer or conductive polymer is heated or thermally treated, one or more side chains are decomposed or removed. The HOS-electrically conductive polymer or HOS-conductive polymer have a higher ordered structure. In some embodiments, the electrically conductive polymer or conductive polymer in a final form, or a HOS- electrically conductive polymer or HOS-conductive polymer, is not soluble in the alcohol-water solvent or water.

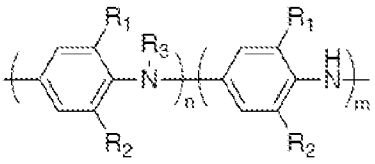
[0008] In some embodiments, the method can be used to apply or coat the binder/electrically conductive polymer-conductive material composite on a surface of an electrode, such as a cathode or anode of a device, such as a battery.

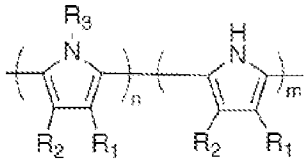
[0009] In some embodiments, the conductive material is a silicon oxide (SiO_x), Si-C, Si, or Si-graphite. In some embodiments, the conductive material is in particle form. In some embodiments, the method results in the electrically conductive polymer coating the conductive material, such as the conductive material in particle form.

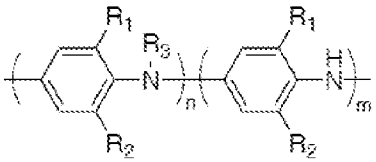
[0010] The electrically conductive polymer, or one or more monomer units of the polymer, comprises one or more chains, wherein each chain comprises one or more ether, methoxy and/or ethoxy groups, wherein there are sufficient ether, methoxy and/or ethoxy groups thereby the electrically conductive polymer is soluble in the alcohol-water solvent or water. In some embodiments, the electrically conductive polymer to a surface, comprising: (a) providing an electrically conductive polymer having the following chemical structure: —A_n—E_m—F_q— (I); wherein A is  ,  , or  ; E and F are each independently  ,  ,  , or  ; R_1 and R_2 are each independently an alkyl chain or oligo ethyleoxide chain or alkyloxide chain of any length between 1-10000 carbon atoms; G and G_1 are each independently —H, —F, —$COOCH_3$, —COOH, or —SO_3CH_3; n + m + q = 1, and representing the relative abundance in the polymer chain; n, m, and q are each independently any number between 0-1; and, R_1 and R_2 are each independently hydroxide terminated or carboxylic acid or carboxylate salt terminated; —Q_n—Q'_m— (II); wherein Q and Q' are each independently is one of the following chemical structures:

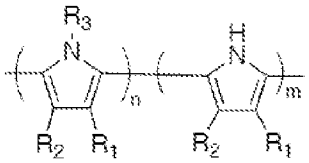


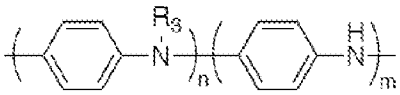


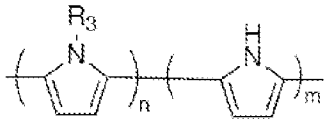


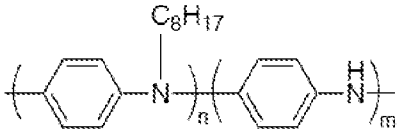


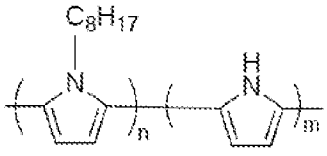


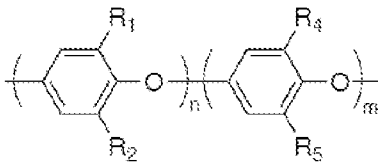


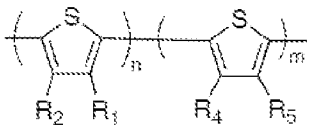


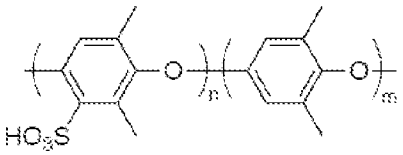




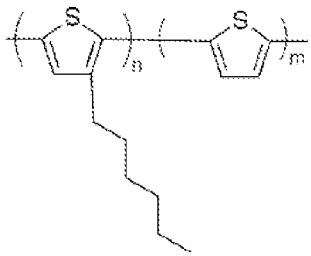


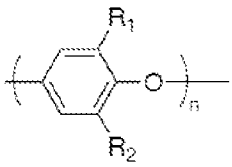


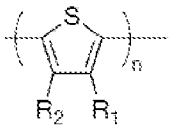


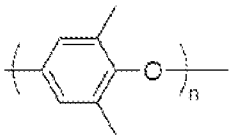


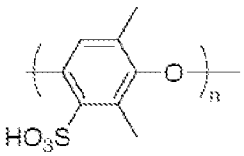
Or Li, Na, K salts



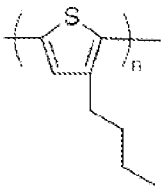


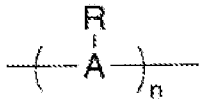
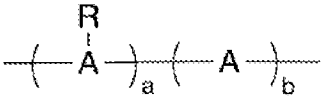
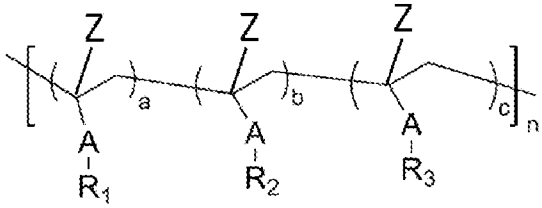




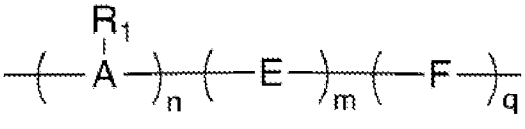
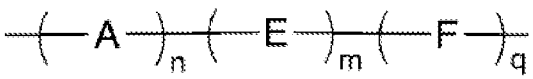


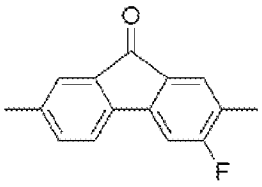
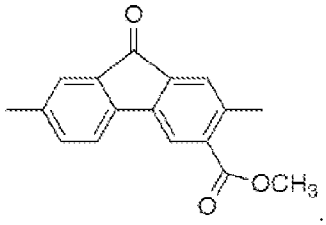
Or Li, Na, K salts

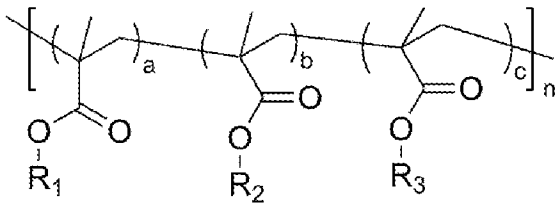
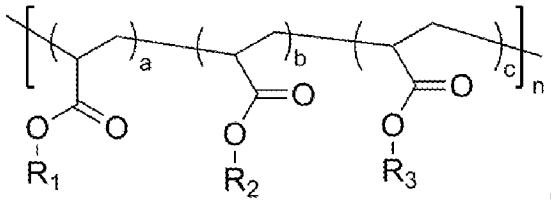
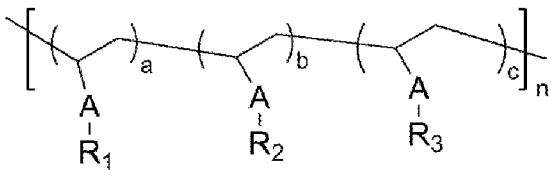
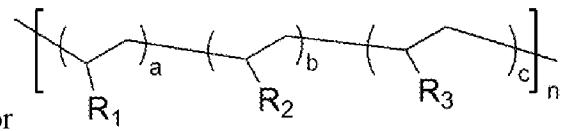


; n is between 1 and 100M; R_1 and R_2 are each independently an alkyl chain or oligo ethyleoxide chain or alkyloxide chain of any length between 1-10000 carbon atoms; and R_1 and/or R_2 can be hydroxide terminated or carboxylic acid or carboxylate salt terminated;  (III) or  (IIIa);  (V); wherein A

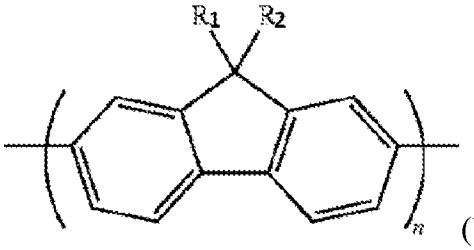
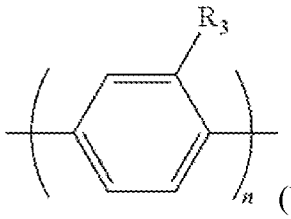
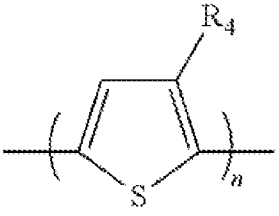
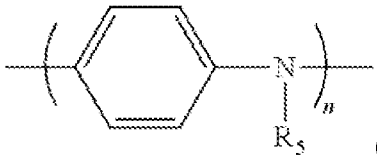
is —COO—, —O—, —NH—, —S—, or a covalent bond; Z is —H or —CH_3; or, $(X)_n$ (V), wherein X is a conjugated homo polymer, a conjugated copolymer, or a linear polymer with conducting conjugated pending group.

[0011] In some embodiments, the electrically conductive polymer has the following chemical structure:  (Ia) or  (Ib).

[0012] In some embodiments, the at least one of E and F is are each independently  or  .

[0013] In some embodiments, the electrically conductive polymer has the following chemical structure:  (IVa);  (IVb);  (IVc); or  (IVd).

[0014] In some embodiments, the electrically conductive polymer has the chemical structure of $(X)_n$ (V), wherein conductive polymer has the following chemical structure:


(Va),

(Vb),

(Vc),

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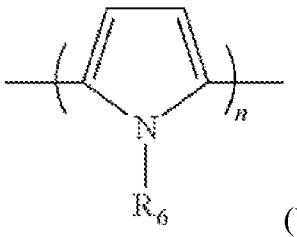
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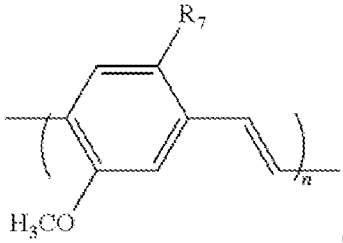
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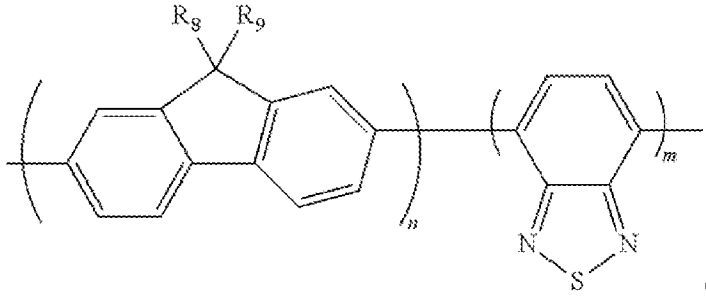
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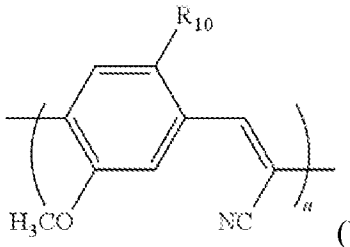
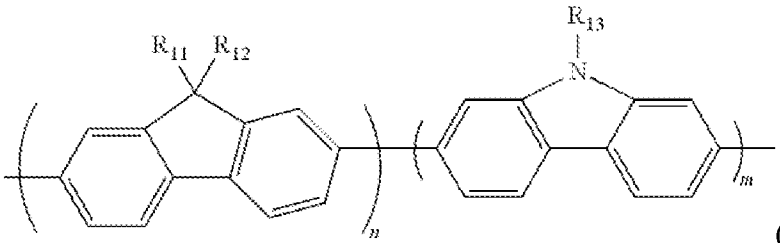
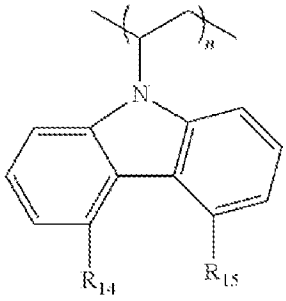

(Vh),

(Vi), or

(Vj).

[0015] In some embodiments, R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, R_{10}, R_{11}, R_{12}, R_{13}, R_{14}, and R_{15} are each independently an alkyl chain or oligo ethyleoxide chain or alkyloxide chain of

any length between 1-10000 carbon atoms. In some embodiments, each side chain is independently any length between 1-1000 carbon atoms. In some embodiments, each side chain is independently any length between 1-100 carbon atoms. In some embodiments, each side chain independently comprises 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 carbon atoms.

[0016] The synthesis of the electrically conductive polymer, and further specific embodiments of the electrically conductive polymer, are taught in PCT International Patent Application No. PCT/US2022/12376 and U.S. Patent Application Ser. No. 18/347,757, both of which are incorporated by refrence in their entireties.

[0017] In some embodiments, the method further comprises heating the alcohol and the polymer to about or at least about 50 ºC, 60 ºC, 70 ºC, 80 ºC, 90 ºC, or 100 ºC, or a temperature within a range of any two preceding values, to dissolve the polymer in the alcohol.

[0018] In some embodiments, any or all of the polymer, conductive material, alcohol, water, or surface is pre-heated to a temperature prior to any of the introducing or applying step.

[0019] In some embodiments, the alcohol is an organic compound having 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10, or a number within a range of any two preceding numbers, carbon atoms. In some embodiments, the alcohol is straight chained or branched. In some embodiments, the alcohol is an organic compound having 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10, or a number within a range of any two preceding numbers, hydroxyl function group. In some embodiments, the alcohol is methanol, ethanol, 1-propanol, 2- propanol, or isopropanol. In some embodiments, the alcohol and water have a ratio to each other about 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, or 9:1, or a ratio within a range of any two preceding values, by weight, by volume, or by mole.

[0020] In some embodiments, the heating step (g) comprises heating to a temperature of about or at least about 200 ºC, 300 ºC, 400 ºC, 500 ºC, 600 ºC, or 700 ºC, or a temperature within a range of any two preceding values.

[0021] The present invention provides for a composition comprising the electrically conductive polymer and an alcohol and water. In some embodiments, the composition is a solution wherein the electrically conductive polymer is dissolved in the alcohol and water. In some embodiments, the composition is a slurry further comprising a silicon oxide. In some embodiments, the composition further comprising one or more active material and/or additive

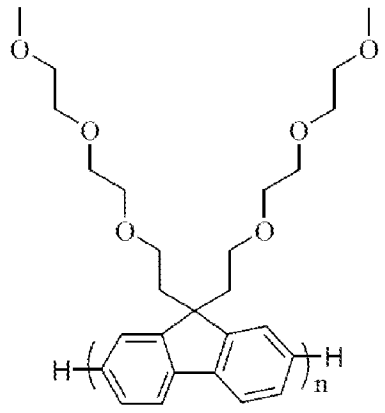
particles.

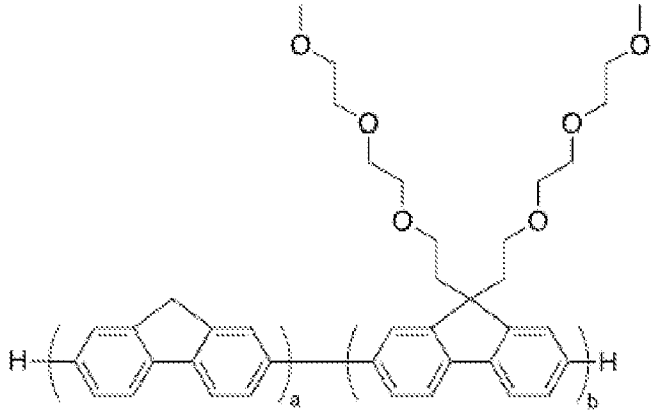
[0022] The present invention provides for a device comprising a current collector applied or coated with the composition of the present invention. In some embodiments, the composition is dried on the current collector. In some embodiments, the dried composition is a film, such as a laminate film, such as a composite laminate film.

[0023] In some embodiments, the method is a low-cost method synthesis of electrically conductive polymer binders, and using environmental benign green solvent to process the conductive polymer binders with Si based electrode materials to achieve the best performance for Si based electrode for lithium-ion rechargeable battery applications.

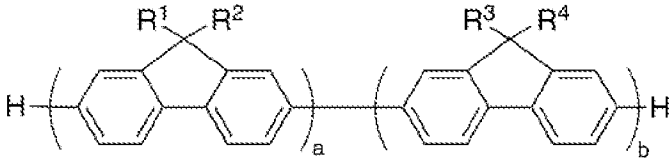
[0024] In some embodiments, the method is used to construct 2 Ah pouch cell development based on PFO binder and SiO negative electrode. In some embodiments, the binders and processes are intended to be used in making high energy density lithium-ion batteries. In some embodiments, the class of binders is made at lower cost compare to the regular PFM conductive polymer binder. In some embodiments, the PFO binder is soluble in an alcohol, such as ethanol, and water, so can be processing in an environmentally friendly slurry process. The present invention provides for a low-cost conductive polymer binder enabled environmentally friendly processing of Si based electrode

[0025] In some embodiments, the electrically conductive polymer is (1) poly(2,7-9,9-(di(oxy-2,5,8-trioxadecane))fluorene) (PFO), which has the following chemical structure:

[0026]  (VIa), wherein n has a value from 1 to 100,000,000;



(VIb), wherein a has a value from 0 to 100,000,000, and b has a value from 1 to 100,000,000; or



(VIc), wherein R^1, R^2, R^3, and R^4 are each independently a $CH_3(OCH_2CH_2)_p–$, $CH_3(CH_2)_q–$, $CH_3O–$, or H–, p has a value from 1 to 10,000, q has a value from 0 to 10,000, p and/or q can vary within the same molecule, a has a value from 0 to 100,000,000, b has a value from 1 to 100,000,000, and the electrically conductive polymer is a random or block co-polymer or homo polymer. A method for synthesizing PFO is shown in Fig. 12.

[0027] In some embodiments, the electrically conductive polymer is a random or block co-polymer or homo polymer.

[0028] In some embodiments, the electrically conductive polymer binder can enable solid-state processing of electrodes. The electrically conductive polymer-based electrode can also be processed solvent free or use very lean solvents in the electrode materials mixing and coating process. electrically conductive polymer can be mixed with Si-based anode materials (and/or graphite, tin, or the like) to homogeneity, and be pressed on current collectors to form a thin electrode laminate on the current collector. Heat treatments can be done to the electrode laminate in the following steps. The electrically conductive polymer can also be used for cathode materials to form cathode laminate both in slurry or in solid-state process. Methods and steps disclosed in Yao, et al., *Energy & Environmental Science*, "A 5 V-class cobalt free battery cathode with high loading enabled by dry coating" (DOI: 10.1039/d2ee03840d), which is incorporated by reference, can be used or adapted in the method of this present invention.

[0029] In some embodiments, the conductive polymer in the final form is useful as a binder and surface protection agent for a Si electrode, or a carbon, Si, Al, Li, or Sn surface. In some embodiments, the thermally treating step comprises heating the composition. In some embodiments, the thermally treating step comprises heating the composition to a temperature ranging from about 100 °C to about 1000 °C. In some embodiments, the thermally or optically treating step takes place in an oxygen free condition, or a control amount of oxygen condition. In some embodiments, the optically treating step comprises contacting or shining high-energy visible light on the composition. In some embodiments, the thermally or optically treating step results in the separating or removing of one or more R group (such as one or more of R_1 - R_{15}), or side chain/functional group, from the conductive polymer. In some embodiments, the device comprises a film of the composition, used in combination with a liquid electrolyte, gel or solid-state electrolytes.

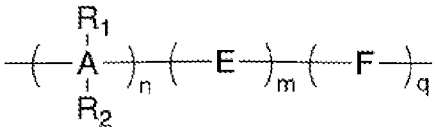
[0030] In some embodiments, the providing step comprises applying or coating the current collector with the composition of the present invention, and optionally drying the composition of the present invention so that the solvent in the composition is separated from the conductive polymer.

[0031] In some embodiments, the providing step comprises heating the composition or conductive polymer such that the conductive polymer is converted into a final form. In some embodiments, the final form of the conductive polymer forms a coating and/or protective layer. In some embodiments, the final form of the conductive polymer forms a coating and/or protective layer covering the active materials particles.

[0032] In some embodiments, the final form of the conductive polymer forms a coating and/or protective layer covering a surface of carbon, Si, Al, Li, or Sn.

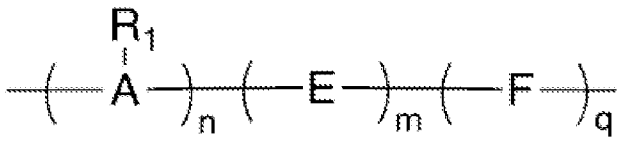
[0033] In some embodiments, the device is a battery, such as a lithium battery, sodium battery, or Mg and/or Zn battery system. In some embodiments, the device is any device in need of a conductive polymer on a current collector that requires ion or electron mobility through the conductive polymer.

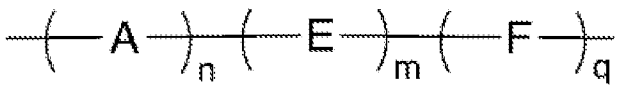
[0034] In some embodiments, the conductive polymer has the following chemical structure:



(I); n+m+q = 1, and representing the relative abundance in the polymer chain; n, m, and q can be any number between 0-1; R_1 and R_2 are an alkyl chain or oligo ethyleoxide chain or alkyloxide chain of any length between 1-10000 carbon atoms; and, R_1 and R_2 can be hydroxide terminated or carboxylic acid or carboxylate salt terminated.

[0035] In some embodiments, chemical structure (I) (also referred to as "the first generic structure") has the following chemical structure:

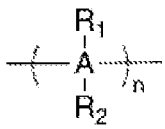
[0036]  (Ia) or

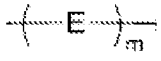
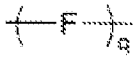
 (Ib).

[0037] The heating or light process can lead to a partial or complete loss of R_1 and R_2 in any composition in the end form. The temperature can range from 100 to 1000 °C. The thermal treatment or light process can be oxygen free or have control amount of oxygen.

[0038] In some embodiments, chemical structure (I) comprises random copolymer(s) or block copolymer(s).

[0039] In some embodiments, chemical structure (I) is transformed, from or to, when thermal treated at high temperature to lose the side chains R_1 and/or R_2.

[0040] In some embodiments, the  segment is one of the chemical structures described in Figure 2.

[0041] In some embodiments, the  and/or  segments are independently one of the chemical structures described in Figure 3 of PCT International Patent Application No. PCT/US2022/12376.

[0042] In some embodiments, chemical structure (I) is described in Figure 4 of PCT

International Patent Application No. PCT/US2022/12376. Examples of poly(9,9-dioctylfluorene-*co*-fluorenone-*co*-methylbenzoic ester) (PFM) and Si composite electrode first generic structure process and usages are described in Figure 4 of PCT International Patent Application No. PCT/US2022/12376. In some embodiments, PFM, or any first generic structure of the polymers, chemical transformation during thermal treatment at about 500 °C. The PFM and Si can be processed into a polymer composite electrode, the pyrolysis at about 500 °C transformed the PFM polymer in the electrode.

[0043] In some embodiments, the conductive polymer has the following chemical structure:

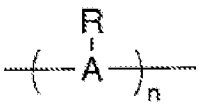
$—Q_n—Q'_m—$ (II) (also referred to as "the second generic structure"); wherein n is between 1 and 100M Dalton; R_1 and/or R_2 are independently an alkyl chain or oligo ethyleoxide chain or alkyloxide chain of any length between 1-10000 carbon atoms; and R_1 and/or R_2 can be hydroxide terminated or carboxylic acid or carboxylate salt terminated. In some embodiments, $—Q'_m—$ is a covalent bond. In some embodiments, n+m = 1, and representing the relative abundance in the polymer chain; n and m can be any number between 0-1.

[0044] In some embodiments, the heating or light process results in partial or complete loss of R_1, R_2, and/or R_3 in any composition in the end form. In some embodiments, the temperature has a range from 100-1000 °C. In some embodiments, the thermal treatment or light process can be oxygen free or have control amount of oxygen.

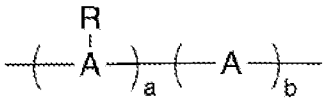
[0045] In some embodiments, chemical structure (II) comprises random copolymer(s) or block copolymer(s).

[0046] In some embodiments, chemical structure (II) comprises one of chemical structures described in Figure 5 or Figure 6 of PCT International Patent Application No. PCT/US2022/12376.

[0047] In some embodiments, the conductive polymer has the following chemical structure:



(III) or



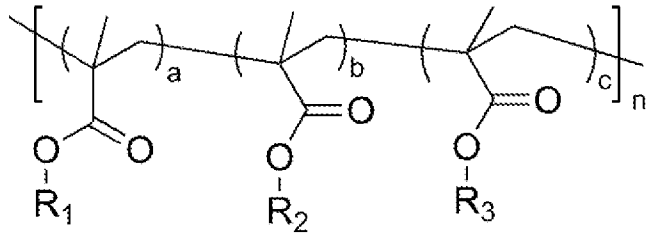
(IIIa) (also referred to as "the third generic structure"); wherein R is an alkyl chain or oligo ethyleoxide chain or alkyloxide chain of any length between 1-10000 carbon atoms. In some embodiments, R can be hydroxide terminated or carboxylic acid or carboxylate salt terminated.

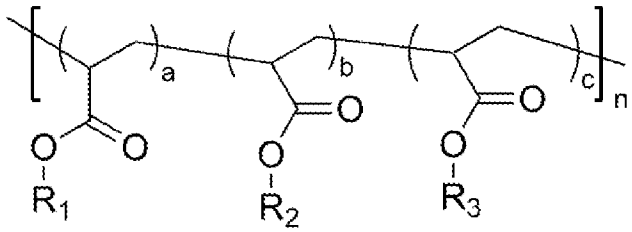
[0048] In some embodiments, chemical structure (III) comprises random copolymer(s) or block copolymer(s).

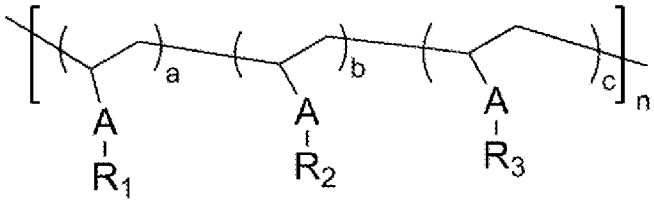
[0049] The main chain with repeating unit of A forms a fully conjugated polymer backbone. Thermal or optical treatment of chemical structure (III) and/or (IIIa) leads to full or partial loss of the side chain R, while preserving the main polymer backbone structures. This process provides unique ion transport properties in the treated polymer film.

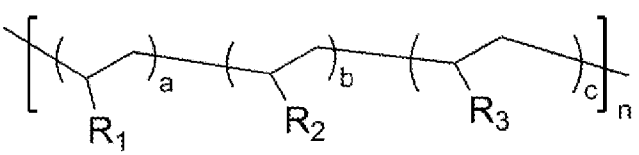
[0050] In some embodiments, the device comprises a lithium ion anode applications, a conductive polymer comprises an n-type of backbone structure. Such conductive polymer include: side chains substituted PPV, side chains substituted polyfluorene, and/or side chains substituted polyphenylene. See Figure 9 of PCT International Patent Application No. PCT/US2022/12376.

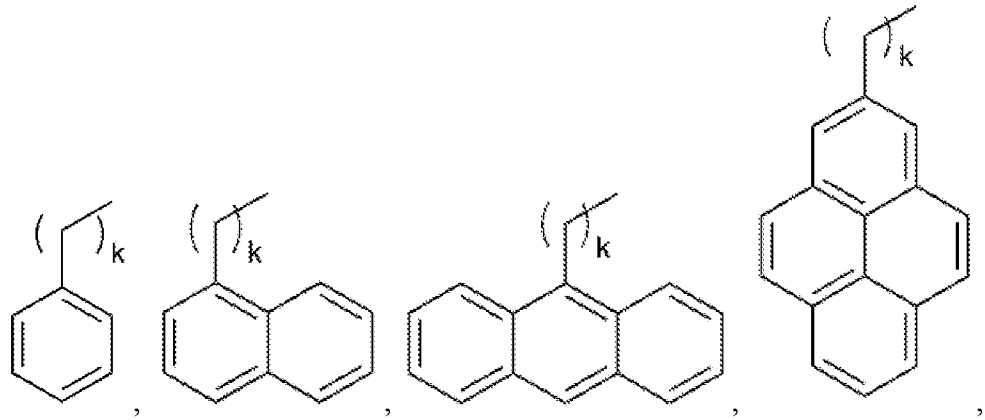
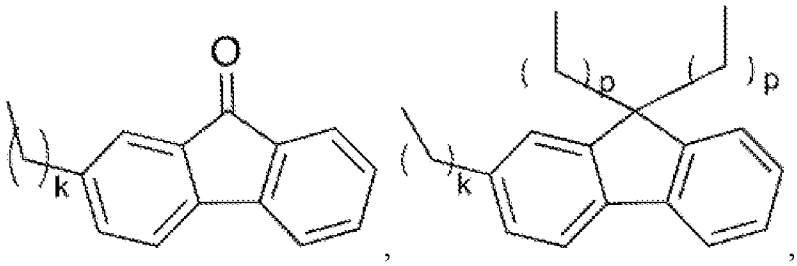
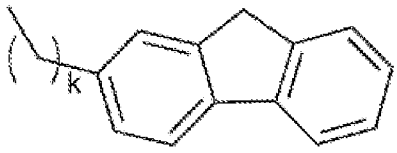
[0051] In some embodiments, the conductive polymer has the following chemical structure:


(IVa);


(IVb);


(IVc); or


(IVd) (also referred to as "the fourth generic structures"). In some embodiments, A is O, N, or S. In some embodiments, R_1 is

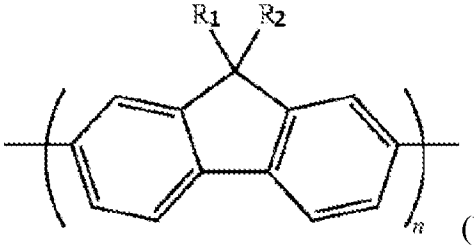




, or —C≡N; wherein k is 0 to 100, the side chain connection to the aromatic moiety can be at any position, p is o to 100, the side chain can be branched. In some embodiments, R_1 is benzene, naphthalene, anthracene, pyrene, fluorenone, or fluorene, or nitrile. In some embodiments, k is 1 to 100, 1 to 50, 1 to 20, or 1 to 10. In some embodiments, p is 1 to 100, 1 to 50, 1 to 20, or 1 to 10. In some embodiments, R_2 is —$(CH_2CH_2O)_mCH_3$, or —$(CH_2)_mCH_3$, wherein m is 0 to 1000. In some embodiments, m is 1 to 100, 1 to 50, 1 to 20, or 1 to 10. In some embodiments, R_3 is H. In some embodiments, a+b+c = 1, and representing the relative abundance in the polymer chain; a, b, and c can be any number between 0-1. See Figure 10 of PCT International Patent Application No. PCT/US2022/12376.

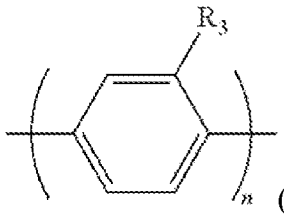
[0052] In some embodiments, chemical structure (IVa) to (IVd) comprises random copolymer(s) or block copolymer(s).

[0053] In some embodiments, the conductive polymer has a chemical structure, and active material and/or additive particles, described in U.S. Patent Nos. 7,960,037 (Liu et al.); 8,852,461 (Liu et al.); 9,077,039 (Liu et al.); 9,653, 734 (Liu et al.); 9,722,252 (Liu et al.); and, PCT International Patent Application No. PCT/US2022/12376 (Liu et al.); which are hereby incorporated by reference.

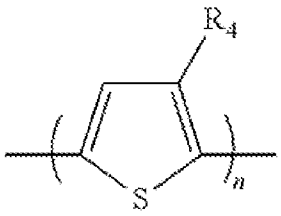
[0054] In some embodiments, the conductive polymer has the following chemical structure: $(X)_n$; wherein X may be a conjugated homo polymer, a conjugated copolymer, or a linear polymer with conducting conjugated pending group. In some embodiments, the conductive polymer has the following chemical structure:



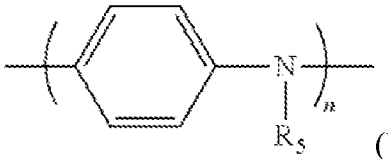
(Va),



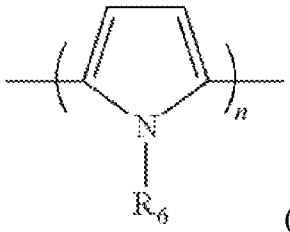
(Vb),



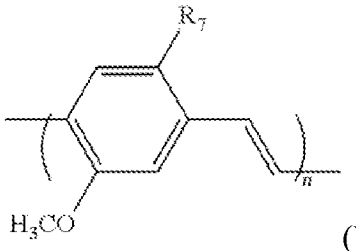
(Vc),



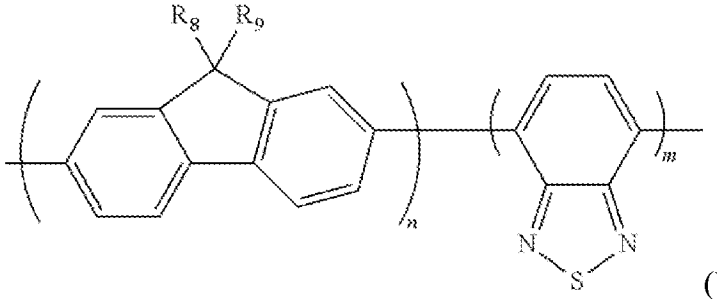
(Vd),



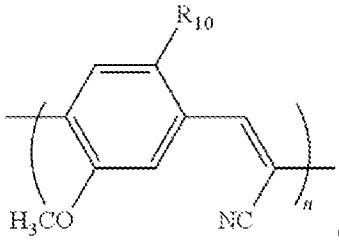
(Ve),



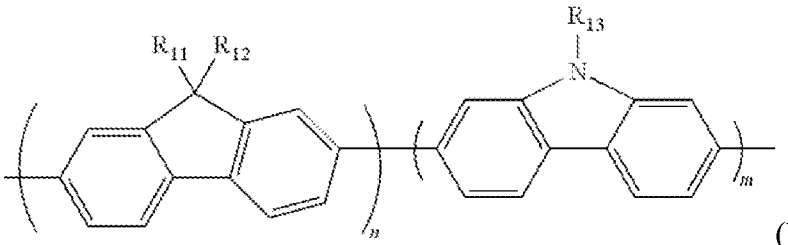
(Vf),



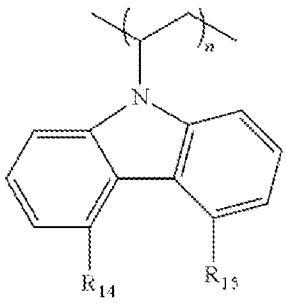
(Vg),



(Vh),

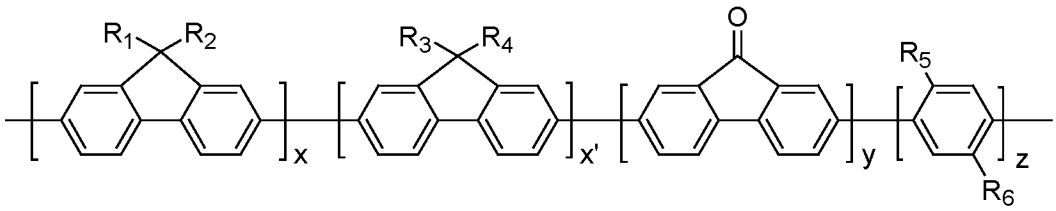


(Vi), or



(Vj).

[0055] In some embodiments, the conductive polymer has the following chemical structure:



PFF'FOB (Vk).

[0056] In some embodiments, x=0, x' and y =>0, and z<=1, and x' + y + z = 1. In some embodiments, R_3 and R_4 are each $(CH_2)_nCOOH$, wherein n = 0 – 8. In some embodiments, R_5 and R_6 are each independently H, COOH, or $COOCH_3$. In some embodiments, the number of COOH groups by copolymerizing x monomer into the main chains. In some embodiments, by adjusting the ratio of x:x', the number of -COOH groups can be controlled without changing the electronic properties of the conductive binders.

[0057] In some embodiments, 0 < x, x', y and z <= 1 and x + x'+ y + z = 1. In some embodiments, R_1 and R_2 are each independently $(CH_2)_nCH_3$, wherein n = 0 – 8. In some embodiments, R_3 and R_4 are each independently $(CH_2)_nCOOH$, wherein n = 0 – 8. In some embodiments, R_5 and R_6 are each independently H, COOH, or $COOCH_3$. In some embodiments, the "x, x'" unit are each independently fluorene with either alkyl or alkylcarboxylic acid at the 9, 9'positions. In some embodiments, the "y" unit is fluorenone. In some embodiments, the H positions of the back bone of fluorenone and fluorene are each independently substituted with one or more of the following functional groups: COOH, F, Cl, Br, SO_3H, or the like groups.

[0058] In some embodiments, the conductive polymer is terminated by H or any other functional group, such as an alkyl, alkenyl, alkynyl, phenyl, aryl, hydroxyl, alkoxyl, halide, amino, thiol, aldehyde, carboxyl, or amide group.

[0059] The conductive polymers of chemical structures (IVa) to (IVj); wherein R_1 - R_{15} are selected from the group consisting of an oligoether group, an alkyl chain having a tertiary amine and an associated counter ion, and an alkyl chain having an SO_3 group and an associated counter ion; wherein said oligoether group terminates with a methyl group or hydroxyl group; and wherein n is between 2 and 1000.

[0060] In some embodiments, the alkyl chain has a tertiary amine and an associated counter ion and the alkyl chain has an SO_3 group and an associated counter ion may comprise 2-20 carbon atoms. R_1 and R_2 may each further comprise methyltriethyleneoxide. R_1 and R_2 may be independently the same group or a different group. In some embodiments, the conductive polymer is poly(2,7-9,9-(di(oxy-2,5,8-trioxadecane))fluorene) ("PFO"). A method of synthesizing PFO is taught in U.S. Patent Nos. 7,960,037 (Liu et al.)

[0061] In some embodiments, the oligoether groups are selected from the group consisting of methyleneoxide, ethyleneoxide, trimethyleneoxide and tetramethyleneoxide.

[0062] In some embodiments, the conductive polymer comprises the chemical structure(s) (Va) to (Vj) comprises random copolymer(s) or block copolymer(s).

[0063] Further specific embodiments of the conductive polymer are described in Tianyu Zhu, et al. "Formation of hierarchically ordered structures in conductive polymers to enhance the performances of lithium-ion batteries" (*Nature Energy*, 8, 129-137, 2023), which is hereby incorporated by reference.

[0064] In some embodiments, the conductive polymer is a PFM. In some embodiments, the device comprises a Si composite electrode inContact with a conductive polymer, such as a first generic structure. In some embodiments, the thermal treatment is oxygen free. In some embodiments, oxygen (partially or entirely) can be used to adjust the treatment process.

[0065] The present invention provides for a method for applying an electrically conductive polymer to a surface, comprising: (a) removing impurities from a used or spent graphite to produce a washed or regenerated graphite; (b) coating the washed or regenerated graphite with an electrically conductive polymer that is soluble in an alcohol-water solvent or water to produce a coated graphite; (c) drying the coated graphite to remove or evaporate part or all of the alcohol and water; and (d) heating or thermally treating the dried coated graphite to a temperature that decomposes or removes part or all side chains of the electrically conductive

polymer or conductive polymer.

[0066] In some embodiments, the used or spent graphite, such as retrieved from a used or spent battery after a plurality of charging and discharging cycles, comprises the weakening of the van der Waals forces between layers within the graphite, mechanical fatigue between the layers within the graphite, and/or increased layer spacings and volume expansion of the graphite. In some embodiments, the used or spent graphite is from a graphite anode.

[0067] In some embodiments, the removing step comprises washing the used or spent graphite with an aqueous wash, and/or an organic solvent wash. In some embodiments, the organic solvent wash uses *N*-methyl pyrrolidone (NMP) and/or toluene. In some embodiments, the washing is carried out with sonification and/or filtration. In some embodiments, the washing is followed by drying to remove the aqueous wash and/or an organic solvent wash from the graphite. In some embodiments, the drying is carried out in a low pressure or vacuum.

[0068] In some embodiments, the heating step comprises heating to a temperature of about or at least about 200 °C, 300 °C, 400 °C, 500 °C, 600 °C, or 700 °C, or a temperature within a range of any two preceding values.

[0069] The present invention provides for a method for enhancing the cycle life of recycled a graphite material from spent lithium-ion devices or batteries via the conductive polymer of the present invention. In some embodiments, the conductive polymer is a coating.

[0070] The present invention provides for a method for the regeneration and reuse of spent graphite anode materials. In some embodiments, the method purifies and revitalizes graphite particles by removing legacy solid electrolyte interphase (SEI) and constructing an artificial conductive polymer-based SEI layer, known as HOS-PFM. This polymer has a conjugated polyfluorene backbone that significantly improves the electrical conductivity and mechanical durability of the regenerated graphite particles. Electrochemical tests involving both half-cells and full cells reveal that regenerated graphite coated with HOS-PFM have a remarkable increase in cycle life and demonstrate the ability to sustain high C-rate charging and discharging. This method provides a simple and effective solution for reclaiming and reusing graphite anodes in battery manufacturing.

BRIEF DESCRIPTION OF THE DRAWINGS

[0071] 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.

[0072] Figure 1. The molecular weight distribution of the produced PFO polymers.

[0073] Figure 2. A) The appearance of 6.7% PFO dissolved in ethanol/water 2:1 mixture at 80 °C, cooled to about 50 °C, and cooled to 25 °C. B) The appearance of fabricated SiOx-PFO electrode using EtOH/H_2O solution. Composition: 200-300 mg SiOx, 100 mg PFO, 1.5 mL EtOH/H_2O (2:1) mixture. PFO was firstly dissolved in hot EtOH then water was added.

[0074] Figure 3. (A) SEM image of SiOx-PFO-400 (processed at 400°C) fabricated from chlorobenzene. The initial weight fraction of PFO is 33%. After thermal treatment, the weight percentage decreased to 19.8%. (B) SEM image of SiOx-PFO-400 fabricated from EtOH/H2O. The initial weight fraction of PFO is 33%. After thermal treatment, the weight percentage decreased to 19.8%.

[0075] Figure 4. A) The capacity evolution and B) Coulombic efficiency evolution of the SiOx-PFO electrode fabricated from chlorobenzene, with different thermal processing temperature. Li||SiOx-PFO half cells were assembled and the areal capacity was around 1.5 mAh/cm^2. Electrolyte: Gen 2. Formation: 0.01V to 1V, C/10; Cycle: 0.05V to 1V, C/3.

[0076] Figure 5. The capacity evolution of the SiOx-PFO-400 electrodes fabricated from different solvents. Electrodes were processed at 400°C. Li || SiOx-PFO-400 half cells were assembled. Electrolyte: Gen 2. Formation: 0.01V to 1V, C/10; Cycle: 0.05V to 1V, C/3.

[0077] Figure 6. Full cell test results. To improve the areal capacity, the PFO was reduced to 25% (after thermal treatment at 400 °C it was 14.3%, and SiOx 85.7%) in the anode electrode. (A) The capacity evolution and (B) Coulombic efficiency evolution of the assembled full cells.

[0078] Figure 7. Controlled thermal decomposition of PFO side chains. A) Structure of PFO. B) The pyrolysis behavior of PFO was characterized by the TGA. Temp ramp rate = 2.5 °C/min, under Argon atmosphere. C) The evolution of PFO ATR-FTIR spectra during the pyrolysis process. D) The surface morphology of pristine PFO and HOS-PFO processed at different temperature, samples were prepared from PFO-chlorobenzene solution.

[0079] Figure 8. A) Cyclic voltammetry study of pristine PFO and PFO-400°C. Scan rate is 0.01 mV/s to ensure complete lithiation of the polymers. B) Potential hold characterization of PFO and PFO-400°C. Potential was scanned from OCV to 0.01V with scan rate at 0.1 mV/s, then hold at 0.01V. C) The relationship between HOS-PFO conductivity and its OCV after lithiation. D, E) The capacity and Coulombic efficiency evolution of the Li||SiOx-PFO half cells. F, G) The surface morphology of SiOx-PFO-400 before and after cycling. (F) The SEM image of the SiOx-PFO-400 before GCPL test. (G) The SEM image of SiOx-PFO-400 after 100 cycles.

[0080] Figure 9. A) The evolution of Small-angle X-ray scattering (SAXS) pattern of PFO dissolved in EtOH/H_2O (10wt%) upon heating. B) The XRD pattern of the freestanding PFO film prepared from chlorobenzene (CB) and EtOH/H_2O mixture. C) The Wide-angle X-ray scattering (WAXS) pattern of PFO prepared from different solvents. D, F) The morphology of PFO dried on silicon wafer, PFO sample was dissolved in NMP and EtOH/H_2O, respectively. E, G) The morphology of PFO-400 on silicon wafer. Before the thermal processing, the PFO was dissolved in NMP and EtOH/H_2O, respectively.

[0081] Figure 10. A) SEM image of SiOx-PFO-400 fabricated from Chlorobenzene. the initial weight fraction of PFO is 33%. After thermal treatment, the w% decreased to 19.8%. B) SEM image of SiOx-PFO-400 fabricated from EtOH/H2O. the initial weight fraction of PFO is 33%. After thermal treatment, the w% decreased to 19.8%. C) The capacity evolution of the SiOx-PFO-400 electrodes. Li||SiOx-PFO-400 half cells were assembled. Electrolyte: Gen 2. Formation: 0.01V to 1V, C/10; Cycle: 0.05V to 1V, C/3. D, E) Full cell tests were conducted, and the capacity evolution and Coulombic efficiency (CE) were monitored. To improve the areal capacity, the PFO% was reduced to 25% (after thermal treatment at 400°C it was 14.3%).

[0082] Figure 12. A method for synthesizing of poly(2,7-9,9-(di(oxy-2,5,8-trioxadecane))fluorene) (PFO).

[0083] Figure 13. A) Protocol for recycling graphite and the appearance of the electrode from spent lithium-ion batteries and new electrode fabricated with regenerated graphite. B) Schematic illustration of graphite particles throughout the regeneration process. C) The HOS formation of PFM by the alkyl chain cleavage during thermal processing at 500°C. D) The thermogravimetric analysis (TGA) result of PFM.

[0084] Figure 14. A) The FT-IR spectra of unwashed graphite as well as regenerated graphite. B) The X-ray diffraction (XRD) patterns of the unwashed graphite, regenerated graphite after solvent washing, as well as the regenerated graphite with HOS-PFM coating.

[0085] Figure 15. A, D) SEM images of regenerated graphite under different magnification. B, E) SEM images of regenerated graphite+PFM composite (after drying in 80°C) under different magnification. C, F) SEM images of regenerated graphite+HOS-PFM composite (after thermal processing at 500°C) under different magnification.

[0086] Figure 16. A) Calculated Li/C molar ratio from the elemental analysis of HOS-PFM samples after lithiation under different potentials. B) Linear sweep voltammogram (LSV) of HOS-PFM in the lithium-ion electrolyte from OCV to 0V (vs. Li/Li^+).

[0087] Figure 17. A, B) Charge-discharge profiles of the Li||regenerated graphite half cells with or without HOS-PFM on the graphite surface at Cycle 1 (A) and Cycle 10 (B). C) Capacity retention of the Li||regenerated graphite half cells with or without HOS-PFM on the graphite surface. D) Coulombic efficiency evolution of the Li||regenerated graphite half cells with or without HOS-PFM on the graphite surface.

[0088] Figure 18. A) Discharge capacity retention of the regenerated graphite||NMC532 full cells with or without HOS-PFM on the graphite surface. B) Coulombic efficiency evolution of the regenerated graphite||NMC532 full cells with or without HOS-PFM on the graphite surface.

[0089] Figure 19. A) The SEM image and elemental mapping results of regenerated graphite anodes after 300 cycles. Scale bar = 20 μm. B) The SEM image and elemental mapping results of regenerated graphite+HOS-PFM anodes after 300 cycles. Scale bar = 20 μm. C) Magnified SEM image and elemental mapping results of regenerated graphite anodes after 300 cycles. Scale bar = 6 μm. D) Magnified SEM image and elemental mapping results of Regenerated graphite+HOS-PFM anodes after 300 cycles. Scale bar = 6 μm.

[0090] Figure 20. Rate capability test of the regenerated graphite||NMC532 full cells with or without HOS-PFM coating on the graphite surface. Charge and discharge processes were conducted at the same C-rates.

DETAILED DESCRIPTION OF THE INVENTION

[0091] 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.

[0092] 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:

[0093] 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.

[0094] 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 an "expression vector" includes a single expression vector as well as a plurality of expression vectors, either the same (e.g., the same operon) or different; reference to "cell" includes a single cell as well as a plurality of cells; and the like.

[0095] 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:

[0096] 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.

[0097] 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.

[0098] The term "about" refers to a value including 10% more than the stated value and 10% less than the stated value.

[0099] 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.

[00100] Other objects, features, and advantages of the present invention will be apparent to one of skill in the art from the following detailed description and figures.

[00101] In some embodiments: the electrically conductive polymer is used in cell fabrication. In some embodiments, the electrically conductive polymer is used in lithium metal electrode or anode-less electrode fabrication. In some embodiments, the electrically conductive polymer is used in cell fabrication. In some embodiments, the device is a Li/PFM500/Au solid-state device. In some embodiments, the device comprises an Au electrode side, a middle round disk that is the gold electrode/substrate, where PFM500 is coated on the opposite side, a plastic ring, and a compressed Li metal. In some embodiments, the device is a Li/PFM500/Au device. In some embodiments, the device is a Na/PFM500/Au solid-state device.

[00102] Examples of different applications of the electrically conductive polymers, such as in battery field, are as follows: (1) The polymers can be dissolved in an alcohol water solvent and mixed with active materials particles and other additive particles to form a slurry. The slurry can be coated on the surface of a current collector and dried into a composite laminate film. The film then be thermal treated to transform into the final form. This

laminate can be used in combination with liquid electrolyte, gel or solid-state electrolytes. (2) The polymers can be dissolved in an alcohol water solvent and coated on to the active materials surface and dried and thermal treated at the selected temperature to transform into the final form to form the coating and protective layer. The coated particles can be used as battery materials. (3) The polymer can be directly coated on a flat surface such as carbon, Si, Al, Li, Sn film surface and be thermal treated to transform into the final form. (4) The usages can be for lithium battery, sodium battery, Mg and Zn battery system. (5) The usages are not limited to battery application, but can be used to any applications need to have ion or electron mobility.

[00103] 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.

[00104] All patents, patent applications, and publications mentioned herein are hereby incorporated by reference in their entireties.

[00105] 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

EXPERIMENTAL PROCEDURE

1. Synthesis of Poly(2,7-9,9 (di(oxy-2,5,8-trioxadecane))fluorene) (PFO)

[00106] In a typical procedure for synthesizing PFO, a 20 mL flask was charged with 2,7-Dibromo-9,9 (di(oxy-2,5,8-trioxadecane))fluorene (2.0 g, 3.15 mmol), triphenylphosphine (82 mg, 0.315 mmol), 99.998% zinc powder-100 mesh (0.65 g, 9.5 mmol), 2,2-dipyridyl (24.5 mg, 0.165 mmol), and nickel chloride (8 mg, 0.065 mmol) under an Argon atmosphere. Subsequently, 2 mL of Dry DMAc was injected using a syringe, and the resulting mixture was stirred at 80 °C for a duration of 3 days. Following cooling to room temperature, the reaction slurry was diluted with 5 mL of additional tetrahydrofuran (THF).

This mixture was then introduced into an 80 mL mixture of methanol and 50% HCl solution (25/75). The resultant polymer pellets, which formed as a precipitate, were collected through centrifugation at 6000 rpm. These pellets were then subjected to a purification process involving repetitive dissolution in THF and subsequent precipitation in water, which was repeated three times. The purified polymer pellets were further treated by undergoing three rounds of dissolution in THF and precipitation in hexanes. The molecular weight of produced PFO was analyzed by gel permeation chromatography (GPC). Mn = 11.0 kDa, PDI = 2.6. ^{1}H NMR (300 MHz, $CDCl_3$) d 2.59 (b, 4H), 2.91 (b, 4H), 3.20-3.60 (m, 22H), 7.50-8.00 (m, 6H). Elemental analysis calc. for C, 0.7101; H, 0.0795; found C, 0.7084; H 0.0800.

2. Electrode Preparation Process

Electrode preparation in Chlorobenzene:

[00107] 100 mg PFO was first dissolved in 1.5 mL of chlorobenzene under ultrasonication for 30 minutes. Then SiOx composite (weight varies from 200 mg to 300 mg, depending on the target PFO weight fraction) was added to the solution and homogenized by continuous stirring. The obtained slurry was then coated on 50 μm-thick copper current collector with a common doctor blade coating method at room temperature. The produced electrode was dried at room temperature for 12 h and further dried by vacuum oven for 12 h.

Electrode preparation in ethanol-water mixture:

[00108] 100 mg PFO was first suspended in 1 mL of 200 PRF ethanol under ultrasonication for 30 minutes. Then the suspension was heated to around 80°C which allows complete dissolution of the PFO polymers. Subsequently, 0.5 mL of pre-heated DI water (80°C) was added to the PFO solutions under stirring, followed by addition of SiOx composite (weight varies from 200 mg to 300 mg, depending on the target PFO weight fraction). The obtained slurry was then maintained at 80°C, before being coated on 50 μm-thick copper current collector with a common doctor blade coating method. Surface was pre-heated to 50°C and the wet gap for doctor blade was controlled at 100 μm or 200 μm. The produced film was dried at 50°C for 1 h and further dried by vacuum oven for 12 h.

[00109] The PFO can be dissolved in moderate concentration in ethanol solution at elevated temperature. The solution remains a homogenous mixture when addition of water to the PFO ethanol solution at 50 °C. We can also use isopropanol/water or 1-propanol/water co-solvent to dissolve PFO. The high boiling point water component can ensure homogeneous processing of the slurry. The coating of the slurry is smooth. The final dried laminate is uniform and defect free. The ratio between alcohol and water can be adjusted to achieve the best overall processing and performance.

Electrode thermal processing:

[00110] SiOx-PFO film were subjected to thermal processing for formation of hierarchically ordered structures. Typically, SiOx-PFO electrodes were placed in tube furnace under argon atmosphere protection. The temperature was ramped to different target temperature (400°C or 500°C) in 2 hours, then held at the target temperature for 10 min. Electrodes (dia. = 9/16'') were collected from the prepared films and stored in argon-filled glovebox before use.

3. Cell assembly

Half cell:

[00111] CR2032 half-cells were assembled in Ar-filled glove box by sandwiching the separator (Celgard 2400) between prepared electrode (HOS-PFO weight% ranges from 19.8% to 16.4% depending on the thermal processing temperature) and lithium metal disk. Gen 2 electrolyte (1.2 M $LiPF_6$ in ethylene carbonate: ethylmethyl carbonate (EC: EMC, 3:7 by weight)) was used as electrolyte. Around 40 μL electrolyte was used for individual cell. Cell formation was performed by cycling between 0.01V to 1.0V at C/10 rate for 3 times. After that, cell was cycled in between 0.05V to 1.0V.

Full Cell:

[00112] Pre-lithiation of SiOx-PFO anodes (HOS-PFO weight% around 16.4%) was performed by half-cell electrochemical method. CR2032 half-cells were assembled in Ar-filled glove box by sandwiching the separator (Celgard 2400) between prepared electrode and lithium metal disk. Cell was cycled in between 0.01V to 1.0V at C/20 rate and C/10 rate. In the last cycle, the cell was charged to 0.6 V to partially withhold lithium in the electrode. The cell was then disassembled in Argon-filled glovebox to obtain the pre-lithiated anode.

[00113] Full cell was assembled by sandwiching the separator (Celgard 2400) between pre-lithiated anode and NMC811 cathode (Areal capacity = 4.0 mAh/cm^2). Gen 2 electrolyte was also used as electrolyte and around 40 μL electrolyte was used for individual cell. Full cell formation was performed by cycling in between 3.0V to 4.1V at C/20 rate and C/10 rate. After that, the cell was cycled in between 3.0V to 4.1V at C/3 rate.

EXAMPLE 2

METHODS AND MATERIALS

Materials

[00114] All chemicals for polymer synthesis were purchased and used without further purification. All materials utilized for the fabrication of the battery were procured from commercial sources. These include micro-sized SiOx particles (m-SiOx) obtained from Shin-Etsu Chemical Co., a lithium chip from MTI Co., Celgard 2400 separator from Celgard Co., a lithium-ion electrolyte consisting of 1.2 M $LiPF_6$ in ethylene carbonate-ethyl methyl carbonate (EC:EMC) with a ratio of 3/7 w/w, specifically known as Gen 2 electrolyte and sourced from Argonne National Laboratory, and a lithium nickel manganese cobalt oxide (NCM811) cathode with a capacity of 4.0 mAh/cm^2, produced by the CAMP Facility at Argonne National Laboratory.

Synthesis of polymer

[00115] In a typical procedure for synthesizing PFO, a 20 mL flask was charged with 2,7-Dibromo-9,9 (di(oxy-2,5,8-trioxadecane))fluorene (2.0 g, 3.15 mmol), triphenylphosphine (82 mg, 0.315 mmol), 99.998% zinc powder-100 mesh (0.65 g, 9.5 mmol), 2,2-dipyridyl (24.5 mg, 0.165 mmol), and nickel chloride (8 mg, 0.065 mmol) under an Argon atmosphere. Subsequently, 2 mL of Dry DMAc was injected using a syringe, and the resulting mixture was stirred at 80 °C for a duration of 3 days. Following cooling to room temperature, the reaction slurry was diluted with 5 mL of additional tetrahydrofuran (THF). This mixture was then introduced into an 80 mL mixture of methanol and 50% HCl solution (25/75). The resultant polymer pellets, which formed as a precipitate, were collected through centrifugation at 6000 rpm. These pellets were then subjected to a purification process involving repetitive dissolution in THF and subsequent precipitation in water, which was repeated three times. The purified polymer pellets were further treated by undergoing three rounds of dissolution in THF and precipitation in hexanes. The molecular weight of produced PFO was analyzed by gel permeation chromatography (GPC). Mn = 11.0 kDa, PDI = 2.6.

Doping and conductivity measurement

[00116] Initially, PFO was dissolved in chlorobenzene to create a 10 wt% solution. Subsequently, 5 μL of this solution was deposited onto the interdigitated electrode and left to air-dry overnight. To eliminate any residual solvent, the interdigitated electrodes underwent a vacuum oven drying process at 80°C for 12 hours. In a two-electrode configuration, lithium foil was positioned on the anode side. The two pins of the interdigitated electrodes were initially short-circuited and then linked to the cathode side via copper wires. The polymer

underwent lithiation at various potentials (from 3.00 V (OCV) to 0.01 V versus Li/Li^+). The electronic conductivity at different doping states was gauged through direct current circuit measurements of the interdigitated electrode. The voltage applied ranged from 20 mV to 100 mV.

[00117] The conductivity of PFO films at different lithiation depth was calculated according to this equation:

$$\sigma_R = \frac{1}{R_e} \times \frac{d}{lh(N-1)}$$

Re: Electronic resistance of the polymer

d: distance of interdigitated digits, 20 um

N: numbers of interdigitated digits, 50

l: length of digits, 0.21 cm

h: thickness of polymer coatings, 15 um

Electrode fabrication

Electrode preparation in Chlorobenzene:

[00118] 100 mg PFO was first dissolved in 1.5 mL of chlorobenzene under ultrasonication for 30 minutes. Then SiOx composite (weight varies from 200 mg to 300 mg, depending on the target PFO weight fraction) was added to the solution and homogenized by continuous stirring. The obtained slurry was then coated on 50 μm-thick copper current collector with a common doctor blade coating method at room temperature. The produced SiOx-PFO electrode was dried at room temperature for 12 h and further dried by vacuum oven for 12 h, before being subjected to thermal processing for formation of hierarchically ordered structures. Typically, SiOx-PFO electrodes were placed in tube furnace under argon atmosphere protection. The temperature was ramped to different target temperature (400°C or 500°C) in 2 hours, then held at the target temperature for 10 min. Electrodes (dia. = 9/16'') were collected from the prepared films and stored in argon-filled glovebox before use.

Electrode preparation in ethanol-water mixture:

[00119] 100 mg PFO was first suspended in 1 mL of 200 PRF ethanol under ultrasonication for 30 minutes. Then the suspension was heated to around 80°C which allows complete dissolution of the PFO polymers. Subsequently, 0.5 mL of pre-heated DI water (80°C) was added to the PFO solutions under stirring, followed by addition of SiOx

composite (weight varies from 200 mg to 300 mg, depending on the target PFO weight fraction). The obtained slurry was then maintained at 80°C, before being coated on 50 μm-thick copper current collector with a common doctor blade coating method. Surface was pre-heated to 50°C and the wet gap for doctor blade was controlled at 100μm or 200 μm. The produced film was dried at 50°C for 1 h and further dried by vacuum oven for 12 h. The thermal processing procedure employed here closely resembled that used for electrodes prepared from chlorobenzene.

Cell assembly and battery cycling

Half Cells:

[00120] CR2032 half-cells (Hohsen Co.) were assembled in Ar-filled glove box by sandwiching the separator (Celgard 2400) between prepared electrode (HOS-PFO weight% ranges from 19.8% to 16.4% depending on the thermal processing temperature) and lithium metal disk. Gen 2 electrolyte (1.2 M $LiPF_6$ in ethylene carbonate: ethylmethyl carbonate (EC: EMC, 3:7 by weight)) was used as electrolyte. Around 40 μL electrolyte was used for individual cell. Cell formation was performed by cycling between 0.01V to 1.0V at C/10 rate for 3 times. After that, cell was cycled in between 0.05V to 1.0V.

Full Cells:

[00121] Pre-lithiation of SiOx-PFO anodes (HOS-PFO weight% around 16.4%) was performed by half-cell electrochemical method. CR2032 half-cells were assembled in Ar-filled glove box by sandwiching the separator (Celgard 2400) between prepared electrode and lithium metal disk. Cell was cycled in between 0.01V to 1.0V at C/20 rate and C/10 rate. In the last cycle, the cell was charged to 0.6 V to partially withhold lithium in the electrode. The cell was then disassembled in Argon-filled glovebox to obtain the pre-lithiated anode. Full cell was then assembled by sandwiching the separator (Celgard 2400) between pre-lithiated anode and NMC811 cathode (Areal capacity = 4.0 mAh/cm^2). Gen 2 electrolyte was also used as electrolyte and around 40 μL electrolyte was used for individual cell. Full cell formation was performed by cycling in between 3.0V to 4.1V at C/20 rate and C/10 rate. After that, the cell was cycled in between 3.0V to 4.1V at C/3 rate.

RESULTS AND DISCUSSION

[00122] Synthesis of Poly(2,7-9,9 (di(oxy-2,5,8-trioxadecane))fluorene) (PFO) (Figure 7A) was conducted through a straightforward Yamamoto coupling reaction, by following a previous literature (Jia, Z.; Zhao, H.; Bai, Y.; Zhang, T.; Lupinacci, A. S.; Minor, A. M.; Liu, G., Solvent processed conductive polymer with single-walled carbon nanotube composites. Journal of Materials Research 2015, 30 (22), 3403-3411). We firstly evaluated the thermal decomposition behavior of PFO, as it was found the electronic conductivity of polyfluorene derivatives could be significant enhanced by selective removal of the bulky moieties and generation of hierarchically ordered structures (HOS) (Zhu, T.; Sternlicht, H.; Ha, Y.; Fang, C.; Liu, D.; Savitzky, B. H.; Zhao, X.; Lu, Y.; Fu, Y.; Ophus, C.; Zhu, C.; Yang, W.; Minor, A. M.; Liu, G., Formation of hierarchically ordered structures in conductive polymers to enhance the performances of lithium-ion batteries. Nature Energy 2023, 8 (2), 129-137). According to the thermogravimetric analysis (TGA) of PFO under Argon atmosphere (Figure 7B), the thermal decomposition began from 350°C and most of the side chains of PFO could be removed at 400°C, corresponding to 49.5% weight retention. Further increasing temperature from 400°C to 500°C resulted in completed loss of the functionalities of PFO and the appearance of produced polymer changed from brown to black color. Meanwhile, attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) analysis of the PFO samples also confirmed this stepwise decomposition. Ramping the temperature to 300°C did not result in significant change of the spectra (Figure 7C). In comparison, the sample processed at 400°C resulted significant reduction of C-H stretching signals ranging from 2800 cm^{-1} to 2900 cm^{-1}, corresponding to the elimination of side chains containing ethylene oxide units. Meanwhile, a new peak around 3040 cm^{-1} was presented, which indicated the formation of C9-H sites of the fluorene ring. Complete side chain decomposition at 500°C was confirmed, as no signals from 2800 cm^{-1} to 2900 cm^{-1} were remained.

[00123] Figure 7. Controlled thermal decomposition of PFO side chains. A) structure of PFO. B) The pyrolysis behavior of PFO was characterized by the TGA. Temp ramp rate = 2.5C/min, under Argon atmosphere. C) The evolution of PFO ATR-FTIR spectra during the pyrolysis process. D) The surface morphology of pristine PFO and HOS-PFO processed at different temperature, samples were prepared from PFO-chlorobenzene solution.

[00124] It came to our interest to further explore the relationship between the thermal processing temperature and the electrochemical characteristics of pristine PFO and HOS-PFO

processed at different temperatures. Resulting from the enhanced π-π orbital overlapping, the HOS-PFO demonstrated magnitudes higher lithiation capabilities than pristine PFO, according to the cyclic voltammetry studies (Figure 8A). Among which, the PFO-500 showed much faster lithiation kinetics as we observed a rapid current decay when holding the potential at 10 mV versus Li^+/Li (Figure 8B), which was likely due to completely removed side chains and unblocked Li^+ movement along the polymer layers.

[00125] Figure 8. A) Cyclic voltammetry study of pristine PFO and PFO-400°C. Scan rate is 0.01 mV/s to ensure complete lithiation of the polymers. B) Potential hold characterization of PFO and PFO-400°C. Potential was scanned from OCV to 0.01V with scan rate at 0.1 mV/s, then hold at 0.01V. C) The relationship between HOS-PFO conductivity and its OCV after lithiation. D, E) The capacity and Coulombic efficiency evolution of the Li||SiOx-PFO half cells. F, G) The surface morphology of SiOx-PFO-400 before and after cycling.

[00126] However, this characteristic is not beneficial for functionating as a stable binder for lithium-ion batteries. Firstly, we used PFO as the binder and chlorobenzene as the solvent to fabricate SiOx-PFO electrodes, and they were processed at 400°C (SiOx-PFO-400) and 500°C (SiOx-PFO-500) to produce in-situ formed HOS-PFO structures surrounding SiOx active materials. In half cell test, the capacity of sample without heating (SiOx-PFO-RT) decay very quickly due to the deficient electronic and ionic transport. Fast capacity fade of the SiOx-PFO-500 was also observed after 10 cycles, resulting from weak adhesion of polyfluorene backbone to the SiOx surface. In comparison, the SiOx-PFO-400 demonstrated unchanged cyclability after 25 cycles, due to partially retained side-chain functionality (Figure 8D, Figure 8E). After cycling, the morphology of SiOx-PFO-400 electrodes was preserved according to SEM images (Figure 8F, Figure 8G), indicating that PFO-400 were still wrapped around the active materials without mechanical failure. It is worth noting that PFO-400 were still provided with decent electronic conductivity, as 7 magnitude conductivity increase from 2×10^{-6} mS/cm to 4.5 mS/cm after lithiation (Figure 8C), suggesting its good capability for interface charge transfer.

[00127] Figure 9. A) The evolution of Small-angle X-ray scattering (SAXS) pattern of PFO dissolved in $EtOH/H_2O$ (10wt%) upon heating. B) The XRD pattern of the freestanding PFO film prepared from chlorobenzene (CB) and $EtOH/H_2O$ mixture. C) The Wide-angle X-ray scattering (WAXS) pattern of PFO prepared from different solvents. D, F) The

morphology of PFO dried on silicon wafer, PFO sample was dissolved in NMP and EtOH/H_2O, respectively. E, G) The morphology of PFO-400 on silicon wafer. Before the thermal processing, the PFO was dissolved in NMP and EtOH/H_2O, respectively.

[00128] Besides chlorobenzene, the PFO could be solvated in many other solvents with lower toxicity, which provided more options for slurry preparation and electrode coating. With the presence of hydrophilic side chains, PFO was able to be swollen in mixtures of ethanol and water (v:v = 2:1) at room temperature (Figure 9A). Further heating the viscous gel to 80°C could break the hydrogen bonding between the polymer chains and solvent molecules, which resulted homogenous solution of PFO. Such as gel to solution phase transformation was also characterized by in-situ SAXS study (Figure 9A). The PFO processed from EtOH/H_2O mixture and chlorobenzene are both crystalline, according to the XRD pattern (Figure 3B) and WAXS results (Figure 9C), suggesting the presence of highly ordered structures prior the thermal processing.

[00129] It was noting that the film-formation behavior of PFO would be distinct when different solvents were used. PFO could generate a smooth and uniform coating on silicon wafer when it was dried from chlorobenzene (Figure 7D). In comparison, micro-sized surface features were observed when PFO film was processed from NMP or EtOH/H_2O (Figure 9D, 9F), which was likely due to the coil-to-globule transition of polymers upon de-solvation. However, these features will not influence the close contact between polymers and electrode active materials, as the following thermal processing and formation of HOS-PFO resulted reorganization of polymers. According to the SEM images of HOS-PFO on silicon wafer, both PFO-400 from NMP and PFO-400 from EtOH/H_2O exhibited a relatively smooth surface without cracking. (Figure 9E, Figure 9G).

[00130] Figure 10. A) SEM image of SiOx-PFO-400 fabricated from Chlorobenzene. the initial weight fraction of PFO is 33%. After thermal treatment, the w% decreased to 19.8%. B) SEM image of SiOx-PFO-400 fabricated from EtOH/H2O. the initial weight fraction of PFO is 33%. After thermal treatment, the w% decreased to 19.8%. C) The capacity evolution of the SiOx-PFO-400 electrodes. Li||SiOx-PFO-400 half cells were assembled. Electrolyte: Gen 2. Formation: 0.01V to 1V, C/10; Cycle: 0.05V to 1V, C/3. D, E) Full cell tests were conducted, and the capacity evolution and Coulombic efficiency (CE) were monitored. To improve the areal capacity, the PFO% was reduced to 25% (after thermal treatment at 400°C it was 14.3%).

[00131] As functional binder for silicon anode, the performance of PFO-400 processed from EtOH/H_2O was comparable to that of PFO-400 from chlorobenzene. According to SEM results, we do see homogenous distribution of SiOx particles in both SiOx-PFO-400 samples prepared from chlorobenzene and EtOH/H_2O. Additionally, similar capacity evolution in half-cell test was observed (Figure 10C). Furthermore, SiOx-PFO-400 anodes with 86 wt% of m-SiOx were fabricated at high loading (3.0 mAh/cm^2) under different solvent condition for full-cell cycling with high-nickel content cathode, NMC811, to evaluate the potential for industrial cell manufacturing. Figure 10D shows the capacity retention of full cells cycling at a rate of 0.33C, after electrochemical pre-lithiation of the anode materials. It was found that the SiOx-PFO-400 from chlorobenzene still retained 86% capacity after 200 cycles, while SiOx-PFO-400 from EtOH/H_2O exhibited comparable performance.

EXAMPLE 3

[00132] Pyrolysis. Side chain composition takes place from 300 °C to 400 °C. Around 1620 cm^{-1}, there is possible formation of new conjugated structures (C=C bond). Around 3000 cm^{-1}: elimination of C-H. See Figure 7.

[00133] Cyclic voltammetry. PFO-400 °C demonstrated significant lithiation doping ability comparing to the PFO without thermal treatment, due to the formation of the higher order structure (HOS) at the molecular level. See Figure 11.

[00134] Half cell. Thermal treatment provided HOS-PFO as a good candidate as conjugated polymer binder. However, the decomposition temperature is controlled at 400 °C, so some side chains are still present for surface adhesion. 500 °C heated sample loses all the side chains moieties, and tends to have lower adhesion, therefore worse performance. PFO was applied as the conductive binder for SiOx. Before thermal treatment, the weight fraction of PFO is 33%. After thermal treatment, this number ranges from 19.8% to 16.4% depending on the temperature. All the electrodes were processed in chlorobenzene. See Figure 4.

[00135] Half cell. After 100 cycles, the SiOx-PFO-400 demonstrated good morphology retention. See Figure 8, Panels F and G.

[00136] Green solvent for PFO processing. In EtOH : H_2O = 2:1 mixture, the PFO could still be well dissolved due to additional hydrogen bonding formation. The PFO can be dissolved in moderate concentration in ethanol solution at elevated temperature. The solution

remains a homogenous mixture when addition of water to the PFO ethanol solution at 50 °C. We can also use isopropanol/water or 1-propanol/water co-solvent to dissolve PFO. The high boiling point water component can ensure homogenous processing of the slurry. The coating of the slurry to laminate is uniform. The dried laminate is also defect free. The ratio between alcohol and water can be adjusted to achieve the best overall processing and performance. See Figure 2.

[00137] Green solvent for PFO processing. SiOx-PFO-400 processed from EtOH/H_2O demonstrated similar morphology and cycling performance to the chlorobenzene processed electrode. The active material is SiOx. It is also can be other types of Si materials, and tin and other alloy compounds. See Figs. 3 and 5.

[00138] Green solvent for PFO processing. Full cell test results. To improve the areal capacity, the PFO was reduced to 25% (after thermal treatment at 400 °C it was 14.3%, and SiOx 85.7%) in the anode electrode. Anode: SiOx-PFO-400 3.5 mAh/cm^2. Cathode: NCM811 LN22009-151-2 4.0 mAh/cm^2. Formation: 1x C/20, 1x C/10. Cycle: C/3, 3.0V to 4.1V. Pre-lithiation: Li || SiOx-PFO-400 °C, 1x C/20, 1x C/10. Final voltage: 0.6V. See Fig. 6.

EXAMPLE 4

Enhancing the Cycle Life of Recycled Graphite Materials from Spent Lithium-Ion Batteries via Conductive Polymer Coating

[00139] In recent years, lithium-ion batteries have been widely used in electric vehicles and electronics. Among most commercial lithium-ion batteries, graphite is used as an anode material because it ensures high voltage coupled with lithium-ion cathode and high capacity. Spent lithium-ion battery anode is difficult to be recycled and revitalized, because the pyrometallurgy process only work well with metals oxide cathode. In addition, even the spent graphite were recovered, it could not be directly applied for new electrode fabrication due to its poor interface conductivity and mechanical disintegration. In this study, we introduced an innovative method for the regeneration and reuse of spent graphite anode materials. Our method purified and revitalized graphite particles by removing legacy solid electrolyte interphase (SEI) and constructing an artificial, elastic and conductive polymer-based SEI layer. This polymer has a conjugated polyfluorene backbone that significantly improves the electrical conductivity and mechanical durability of the regenerated graphite particles.

Electrochemical tests involving both half-cells and full cells revealed that regenerated graphite coated with HOS-PFM showed a remarkable increase in cycle life and demonstrated the ability to sustain high C-rate charging and discharging. We suggest that this method could provide a simple and effective solution for reclaiming and reusing graphite anodes in battery manufacturing.

INTRODUCTION

[00140] With growing concerns about climate change and global energy crisis, fuel vehicles are increasingly replaced by electrical vehicles. Consequently, as an essential component of electrical vehicles, the demand of lithium-ion batteries (LIBs) substantially increases. The global lithium-ion batteries market value is predicted to reach $139 billion by 2029 [1]. However, the production of the lithium-ion batteries and the generation of electrical waste after their lifespan can cause significant natural resource exhaustion [1, 2]. More than 11 million tons of LIBs would be discarded between 2017 and 2030. Mistreatment of the spent LIBs would release pollutants such as heavy metals and toxic lithium salts to environment [1-3]. Therefore, recycling spent lithium-ion batteries become an urgent need to reduce material waste and converse resources and energy [4, 5].

[00141] Whereas lithium-ion battery industries have been actively engaged in recycling cathode materials such as $LiCoO_2$ (LCO), $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ (NCM111) and $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM622) [6], the progress of developing recycling strategies for anodes materials, particularly the most commonly used graphite, has not received comparable attention [1, 7, 8]. Graphite is the most classical candidate for the anode material in LIBs, owing to its mechanical and electrochemical stability, high conductivity, and low cost. Nevertheless, not all grades of natural and synthetic graphite are suitable for direct application in LIBs, and the manufacture of battery-grade graphite usually involves a complex and energy intensive process [9]. Refabricating electrodes with recycled graphite offers a more economically viable and environmentally sustainable solution.

[00142] Noteworthily, the graphite materials retrieved from spent batteries cannot be directly utilized in the production of new electrodes [10, 11]. During extended charging and discharging cycles, the repeated processes of lithium-ion intercalation and delamination can alter graphite structure [10]. Specifically, the weakening of the van der Waals forces between graphite layers induces mechanical fatigue, resulting in increased layer spacings and volume

expansion of graphite particles [12]. To ensure that the retrieved graphite materials can be reapplied in LIBs, several methods have been developed for graphite purification and regeneration with a universal goal to remove impurities and restore crystal lattice. The common pyrometallurgical process for recycling cathode materials is also one of the classical methods for graphite recycling, which includes inert atmosphere roasting and graphitization, followed by ultrasonic vibration or sieving to remove the current collector residues [13, 14]. However, the multiunit operation and high energy consumption raise the financial costs thus limit the application of this method [15]. Additionally, the hydrometallurgical process such as acid leaching is recognized as a graphite recycling method due to its low energy consumption and high recovery efficiency [7, 16, 17]. In acidic aqueous solutions, lithium salts and solid electrolyte interphase (SEI) films could be extracted from anode materials. Similarly, Jegan Roy et al. developed a bioleaching approach using the microorganism *A. ferrooxidans* to oxidize the cathode materials, enabling their separation from graphite [8]. Nevertheless, traditional hydrometallurgical process without high-temperature graphitization does not restore the crystal lattice or address the structural damage of the spent graphite, which limits the electrochemical durability of the recycled graphite materials.

[00143] Alternatively, instead of using high-temperature treatment (>1000°C) to repair graphite structure, introducing artificial SEI via surface coating presents another universal and straightforward approach to address the surface defects and mechanical fatigue of spent graphite [18]. Compared to pristine graphite, surface modification is more critical for spent graphite, as its exposed surface structure is prone to collapse if without a protective coating layer [5]. Among the artificial SEI candidates, electronic and ionic conductive polymers have been utilized as battery components owing to their elasticity, versatility, and processibility. For instance, Luo et al. developed a three component (polymer-salt, ionic liquid, and electron-rich additive) ionic-conductive polymer for sodium-ion batteries to achieve accelerated ion conduction [19]. Similarly, Li et al. employed a polymer-blend coating to serve as an artificial solid electrolyte interphase for lithium-ion battery anodes [20]. In our previous study, we developed poly(9,9-dioctylfluorene-*co*-fluorenone-*co*-methylbenzoic ester) (PFM) as a multifunctional conductive polymer designed for high energy density silicon anodes [21, 22]. However, merely randomly distributing PFM does not provide stable coverage surrounding the graphite particles and may still cause the retrieved graphite particles to disintegrate. One way to address this issue is to construct hierarchically ordered structures (HOS) in conductive polymer through thermal treatment. During the thermal

pyrolysis, the alkyl chains on PFM cleave, and the resulting HOS-PFM provides a tightly bound shell for retrieved graphite particles. With highly ordered structures, HOS-PFM further enhances the conductivity of the retrieved graphite particles [22]. Hence, by implementing surface treatment with polymer coating and thermal processing, we can improve the mechanical strength and conductivity of the spent graphite, and the resulting graphite materials with thin coating of HOS-PFM can be refabricated into new electrodes for batteries.

[00144] In this study, we developed a simple process to recycle spent graphite using aqueous wash and organic wash with *N*-methyl pyrrolidone (NMP) and toluene, followed by surface coating with the conductive polymer HOS-PFM via tape casting and thermal processing of PFM (Figure 13). The polymer coating served as a protective layer of recycled graphite particles and a charge transport agent to enhance conductivity of the graphite anode material (Figure 13).

METHODS

Materials and Characterization:

[00145] Polyvinylidene fluoride (PVDF, M_W = 534 kDa) and chlorobenzene (CB) were purchased from Sigma-Aldrich and used as received; PFM was synthesized according to our previous report [21]. Spent lithium-ion batteries for graphite recycling were collected from General Motors. Acetylene black (Denka black) was purchased from Denka Co. The components for CR2032 coin-cell assembly included lithium chip (MTI Co.), Celgard 2400 separator (Celgard Co.), lithium-ion electrolyte (1.2 M $LiPF_6$ in ethylene carbonate-ethyl methyl carbonate (EC-EMC) = 3/7 w/w from Argonne National Laboratory), CR2032 Standard Kits (Hohsen Co.), and NMC532 cathode (1.1 mAh/cm^2, made by CAMP Facility).

[00146] Thermogravimetric analysis (TGA) of PFM was conducted via the thermal analyzer from TA instruments under nitrogen atmosphere. The ramping rate for the TGA measurement was 5°C/min. X-ray diffraction (XRD) patterns were obtained through the Bruker D8 Advance X-ray Diffractometers with a Cu tube ($\lambda_{K\alpha}$ = 0.15418 nm). Scanning Electron Microscopy (SEM) was conducted via the JEOL JSM-7500F Field Emission Scanning Electron Microscope. Elemental mapping of the electrodes was performed at Zeiss Gemini Ultra-55 Analytical Field Emission Scanning Electron Microscope coupled to a Bruker X-Ray Energy Dispersive Spectrometer (X-Ray EDS). The Fourier Transform Infrared (FT-IR) spectra was obtained from Thermo-Fischer Nicolet iS50 FTIR spectrometer.

Battery performance was evaluated by Maccor Cell Testers.

Reclaim of spent graphite anode:

[00147] Spent graphite material was mechanically scraped off from the spent anode current collector. The collected electrode materials were sequentially treated with solvent washing by deionized water, NMP and toluene, assisted by sonication. The final suspension was filtered, and the solids were dried at 80°C under vacuum for 15 hours.

Polymer coating of graphite:

[00148] The retrieved graphite was coated with PFM following the procedure below. Firstly, a chlorobenzene solution of PFM polymer (2 wt.%) was prepared. Then the recycled graphite particles were ground and mixed with the PFM solution, with a final weight ratio of 50:1 graphite: PFM. The powder mixture was dried at 80°C under vacuum for 15 hours to form regenerated graphite+PFM. Thermal treatment of polymer-coated graphite was carried out at 500°C under argon flow, resulting in the regenerated graphite+HOS-PFM composite.

Electrode fabrication:

[00149] A slurry of PFM-coated graphite, Denka Black (DB), and PVDF was prepared in NMP, with a weight ratio of graphite: DB: PVDF 92:2:6. The slurry was coated on copper foil using a doctor blade with a final areal loading of 0.8-1.0 mAh/cm^2. The electrode was thoroughly dried under vacuum before use.

Coin cell assembly:

[00150] CR2032 coin cells were assembled in an argon-filled glovebox. For the half cells, the graphite electrode (14.3 mm diameter disk) and lithium chip counter electrode (16 mm diameter) were assembled in a cell with Celgard 2400 separator and 60 μL lithium-ion electrolyte. For the full cells, the graphite anode (14.3 mm diameter disk) and the cathode NMC 532 electrode (12.7 mm diameter) were assembled in a cell with Celgard 2400 separator and 60 μL lithium-ion electrolyte.

Battery cycling:

[00151] For the half-cell testing, the assembled cells were cycled at 0.1 C between 0.01-1.0 V (vs. Li/Li^+) at 30°C. For the full cell testing, the assembled cells were cycled at

0.04 C for three cycles, 0.1 C for two cycles, 0.2 C for two cycles, and 0.33 C for 300 cycles between 3.8-4.1 V (vs. Li/Li^+) at 30°C. The C-rate was calculated based on the theoretical capacity upon a full lithiation of graphite. For the rate testing, the assembled cells were cycled at 0.04 C for three cycles, 0.1 C for three cycles, 0.2 C for three cycles, 0.33 C for three cycles, 1.00 C for three cycles, and 2.00 C for three cycles.

Elemental Analysis of the HOS-containing HOS-PFM Samples at Different Lithiation Stage:

[00152] For each sample, a 5 mg sample of PFM was coated onto a stainless-steel spacer and thermally processed at 500°C to obtain HOS-PFM. These samples were then assembled into Li||HOS-PFM coin cells and underwent lithiation under various voltages. For HOS-PFM-OCV, the sample was assembled without lithiation (OCV stands for open circuit voltage). For HOS-PFM-0V, the sample was reduced to 0V (vs. Li/Li^+) using linear sweep voltammetry (LSV) at a rate of 0.1 mV/s and then held at 0V for 24 hours. Other samples (HOS-PFM-0.01V, HOS-PFM-0.05V, HOS-PFM-0.1V, HOS-PFM-0.2V, HOS-PFM-0.3V, HOS-PFM-0.4V, HOS-PFM-0.5V) were prepared by modifying the target voltage for lithiation accordingly.

[00153] Post-lithiation, the HOS-PFM samples were washed with anhydrous ethyl methyl carbonate (EMC) and digested in a solution containing 3% w/v HCl and 1% w/v HNO_3 for subsequent elemental analysis. This analysis was conducted with a Perkin Elmer Inductively Coupled Plasma (ICP) Optima 7000 DV Spectrometer. Standard solutions for ICP, with concentrations ranging from 0.01 ppm to 1000 ppm, were prepared by diluting lithium and phosphorus stock solutions purchased from VWR. Yttrium solution was used as an internal standard, and emission measurements were taken at wavelengths of 670.784 nm and 610.362 nm for lithium, and 213.617 nm and 214.914 nm for phosphorus.

RESULTS AND DISCUSSION

Recovery of Graphite and Construction of Polymer Coating

[00154] The failure of the graphite anodes in LIBs is primarily caused by continuous consumption of electrolytes followed by the formation of an SEI on graphite particle surfaces [23]. Although the inner dense SEI layer consisting of inorganic-rich lithium salts is chemically stable and beneficial for surface passivation, the outer layer containing loose organic oligomers derived from ring-opening polymerization of carbonates is primarily

insulating and known as poor SEIs [24]. According to the FT-IR spectra (Figure 14, Panel A), the unwashed graphite showed significant peaks around 3300 cm^{-1} (O-H stretching) and 1630 cm^{-1} (C=O stretching), indicating the presence of the SEI layer from the decomposition of carbonate-based electrolytes. Additionally, characteristic PVDF signals were observed around 1175 cm^{-1} and 840 cm^{-1}. Therefore, we began by cleaning the reclaimed graphite with distilled water to dissolve the lithium salts in the SEI. Furthermore, sequential washes with NMP and toluene were performed to remove the PVDF binder residues (Figure 13). The successfully purified material (regenerated graphite) was confirmed by FT-IR (Figure 14, Panel A).

[00155] Benefitted from the flexible alkyl chains, PFM has excellent solubility and processability in chlorobenzene [22]. Hence, regenerated graphite particles were evenly blended with PFM solution via slurry mixing, and no polymer aggregation was shown in the SEM images of regenerated graphite+PFM composite (Figure 15, Panels B and E). After thermal treatment of the regenerated graphite+PFM composite at 500°C, the alkyl chains on the polymer decompose (Figure 13), leading to possibly increased polyfluorene backbone alignment as well as improved electronic conductivity [22]. We tracked the (002) diffraction peak of graphite related to the stacking layer direction along the *c*-axis (Figure 14, Panel B). It was found the thermal processing did not alter the crystal structures of regenerated graphite. Meanwhile, the retained morphology and dispersity of regenerated graphite after thermal processing were confirmed by SEM characterization (Figure 15, Panels C and F).

[00156] It is worth mentioning that the HOS-PFM polymer layer surrounding the graphite particles are ionic conductive [22], and it will not block the lithium pathways towards graphite particles. This was further evidence by elemental analysis via ICP-OES (Figure 16, Panel A). Significant quantities of lithium were detected in HOS-PFM samples after potential hold under various voltages ranging from 0V to 0.4V, whereas the amount of phosphorus was lower than the detection limit of the instrument (0.01 ppm). Among these samples, a greater amount of lithium was found in the sample under potential hold at a lower voltage: HOS-PFM-0V sample has a C/Li ratio of 0.28, and the quantities of Li were lower than the detection limit in those samples that were lithiated under voltages greater than 0.5V. This result aligns with the linear sweep voltammetry result of Li||HOS-PFM half cells (Figure 16, Panel B). As the voltage decreased from OCV to 0V, the current increases accordingly, which corresponds to the amount of lithium ion diffused into the conductive polymer.

Therefore, HOS-PFM provides an electronic conductive and ionic conductive artificial SEI layer at the surface of regenerated graphite particles.

[00157] Electrochemical Testing of Regenerated Graphite Samples

[00158] To evaluate the effect of polymer coating of HOS-PFM on the regenerated graphite, half-cells were assembled with the regenerated graphite sample and regenerated graphite+HOS-PFM sample, both with lithium metals as the counter electrode. The regenerated graphite anode without polymer coating demonstrated specific capacities of 342 mAh/g at 0.1 C (Figure 17, Panel C) and coulombic efficiency of 99.60% after 30 cycles (Figure 17, Panel D). In comparison, the regenerated graphite+HOS-PFM anode exhibited higher capacities of 353 mAh/g at 0.1 C (Figure 17, Panel C) and Coulombic efficiency of 99.79% after 30 cycles (Figure 17, Panel D). Anodes coated with HOS-PFM achieved stable capacity at an earlier cycle compared to cells without coating, demonstrating that the role of HOS-PFM in interface stabilization (Figure 17, Panels A-C).

[00159] The full cell results further confirmed the improvement in regenerated graphite performance derived from HOS-PFM coating. In regenerated-graphite||NMC532 full cell testing at a rate of 0.33C, cells with regenerated graphite+HOS-PFM anode exhibited an average Coulombic efficiency of 99.92% for the first 300 cycles, which was higher than that of the control cells made without conductive polymer coating (99.82%) (Figure 18, Panel B). The retention rates for cells with and without HOS-PFM coating at the 200^{th} cycle were calculated with respect to the 7^{th} cycle (which was the first cycle at C/3). On average of three trials, the cells without HOS-PFM coating showed a retention rate of 82.9%, while those with the coating demonstrated a higher retention rate of 86.6% (Figure 18, Panel A). It is worth noting that the performance improvement of regenerated graphite should be exclusively resulting from the introduction of HOS-PFM coating, as the thermal processing itself did not change the crystalline structure of graphite, which was reflected by the XRD results (Figure 14, Panel B).

[00160] To better understand the role of HOS-PFM at the anode-electrolyte interface, we characterized the morphology of cycled anodes via SEM coupled with elemental mapping (Figure 19). From the results, the cycled regenerated graphite anode (Figure 19, Panels A and C) exhibited rough and non-uniform surface morphology with many small particles due to the deposition of electrolyte decomposition products, which echoes well with previous reports

[25, 26]. The elemental mapping results demonstrated that the small particles were fluorine-rich, suggesting that they were derived from the decomposition of $LiPF_6$ salt. In comparison, the cycled regenerated graphite+HOS-PFM anode (Figure 19, Panels B and D) exhibited a relatively smooth surface feature, with significantly reduced oxygen and fluorine signals that may result from SEI production. The fluorine regions in cycled regenerated graphite+HOS-PFM were primarily located surrounding the graphite particles, indicating it was mainly attributed to the PVDF binder rather than the SEI derived from $LiPF_6$ decomposition. These SEM results provided additional evidence that the furthermore polymer coating acts as a protective layer to the flaws and surface defects of the regenerated graphite, preventing excessive electrolyte decomposition that significantly reduce the Coulombic efficiency during the cycling.

[00161] The HOS-PFM coating around the graphite particles significantly enhanced the conductivity of regenerated graphite, facilitating efficient charge and discharge of the regenerated graphite at high C-rates (Figure 20). Both cells, with and without HOS-PFM coating, delivered over 85% capacity during cycling at 1C. However, the cells using regenerated graphite+HOS-PFM anodes consistently showed higher capacities across various C-rates, ranging from C/25 to 2C. Over 15.3% of capacity improvement was achieved by introducing HOS-PFM coating on regenerated graphite anode at 1C, which can be attributed to reduced SEI formation and improved conductivity.

CONCLUSION

[00162] We presented a new method for effectively regenerating and reusing graphite anode materials from spent LIBs. The process involves purifying and revitalizing graphite particles through aqueous and organic solvent wash to remove SEI and binder residue, followed by surface coating of a conductive polymer layer with a conjugated polyfluorene backbone, HOS-PFM. This approach enhances the electrical conductivity and mechanical strength of graphite particles. Both half-cell and full-cell electrochemical tests demonstrated that HOS-PFM improves the cycle life of regenerated graphite and enables the material to charge and discharge at high C-rates. The full cells with regenerated graphite+HOS-PFM anode achieved an average Coulombic efficiency of 99.93% and a retention rate of 86.6% at 200^{th} cycle, whereas the full cells without the polymer coating has an average Coulombic efficiency of 99.82% and a retention rate of 82.9%. The SEM and elemental mapping analyses of post-cycling anodes showed that the conductive polymer layer restored the

structure of the regenerated graphite and prevented excessive SEI formation. We believe this can serve as a facile strategy for reclaiming and reusing graphite anodes in the battery industry.

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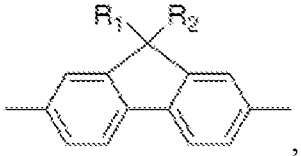
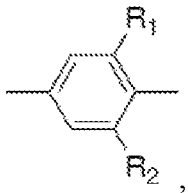
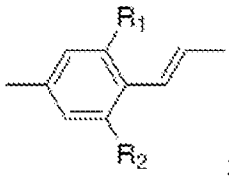
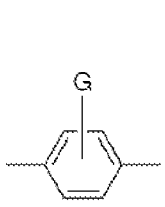
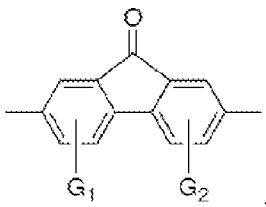
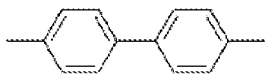
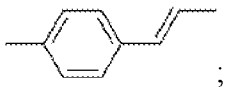
[00164] While the present invention has been described with reference to the specific embodiments thereof, it should be understood by those skilled in the art that various changes may be made and equivalents may be substituted without departing from the true spirit and scope of the invention. In addition, 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.

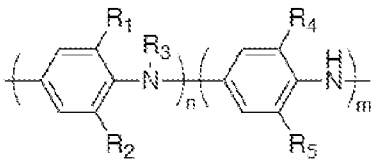
What is claimed is:

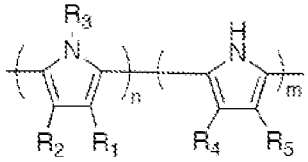
1. A method for applying an electrically conductive polymer to a surface, comprising: (a) providing an electrically conductive polymer, or one or more monomer units of the polymer, comprising one or more chains, wherein each chain comprises one or more ether, methoxy and/or ethoxy groups, wherein there are sufficient ether, methoxy and/or ethoxy groups thereby the electrically conductive polymer is soluble in the alcohol-water solvent or water; (b) introducing an alcohol to the polymer to form a solution; (c) introducing water to the solution; (d) adding a conductive material to the solution to produce a slurry; (e) applying the slurry to a surface; (f) drying the slurry applied to the surface to evaporate part or all of the alcohol and water; and (g) heating or thermally treating the binder to a temperature that decomposes or removes part or all side chains of the electrically conductive polymer.

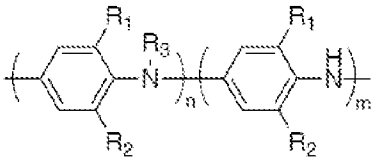
2. The method of claim 1, wherein the electrically conductive polymer or conductive polymer resulting from step (g) is not soluble in the alcohol-water solvent or water.

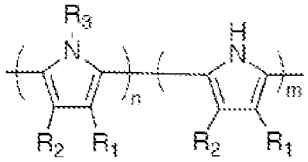
3. The method of claim 1, wherein the electrically conductive polymer or conductive polymer has the following chemical structure: —A_n—E_m—F_q— (I); wherein A is  ,  , or  ; E and F are each independently  ,  ,  , or  ; R_1 and R_2 are each independently an alkyl chain or oligo ethyleoxide chain or alkyloxide chain of any length between 1-10000 carbon atoms; G and G_1 are each independently —H, —F, —$COOCH_3$, —COOH, or —SO_3CH_3; n + m + q = 1, and representing the relative abundance in the polymer chain; n, m, and q are each independently any number between 0-1; and, R_1 and R_2 are each independently hydroxide terminated or carboxylic acid or carboxylate salt terminated; —Q_n—Q'_m— (II); wherein Q and Q' are each independently is one of the following

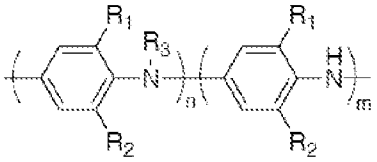
chemical structures:

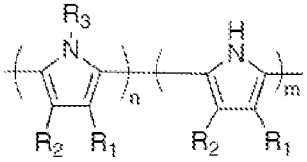


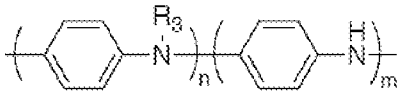


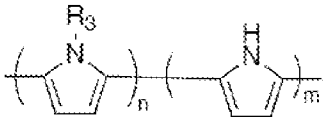


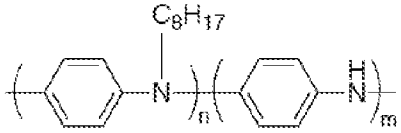


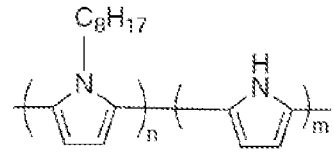


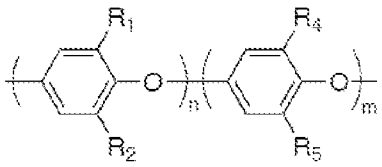


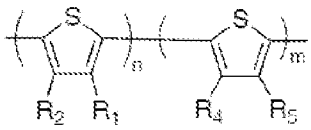


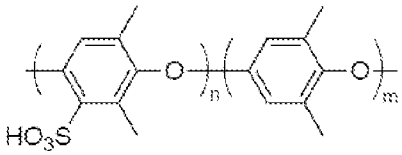




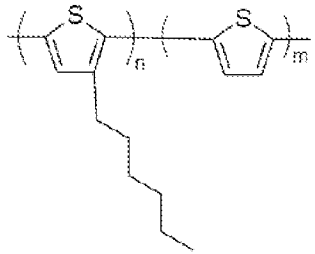


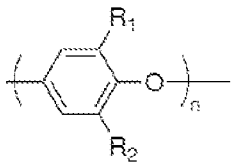


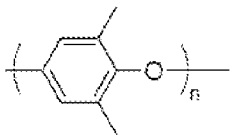


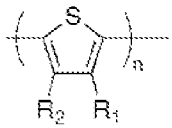


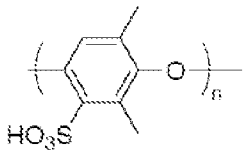
Or Li, Na, K salts

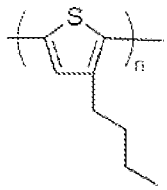




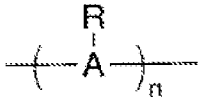
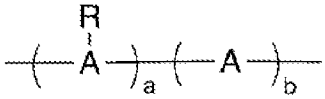


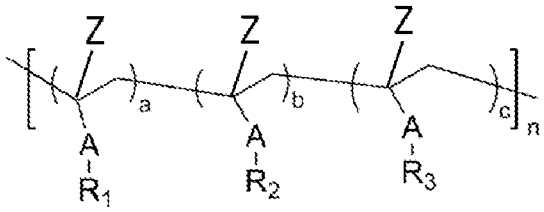






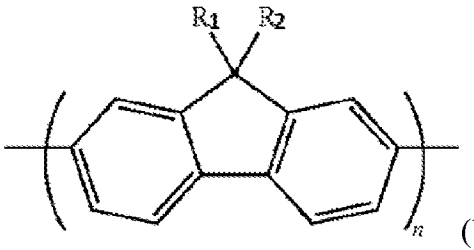
Or Li, Na, K salts

; n is between 1 and 100M; R_1 and R_2 are each independently an alkyl chain or oligo ethyleoxide chain or alkyloxide chain of any length between 1-10000 carbon atoms; and R_1 and/or R_2 can be hydroxide terminated or carboxylic acid or carboxylate salt terminated;  (III) or  (IIIa);

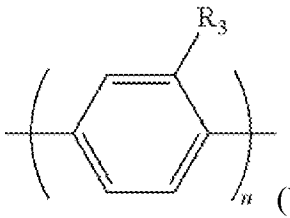


(V); wherein A is —COO—, —O—, —NH—, —S—, or a covalent bond; Z is —H or —CH_3; or, $(X)_n$ (V), wherein X is a conjugated homo polymer, a conjugated copolymer, or a linear polymer with conducting conjugated pending group.

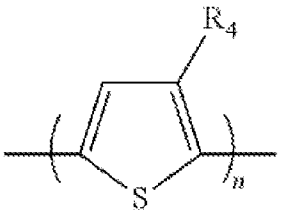
4. The method of claim 3, wherein the conductive polymer has the following chemical structure:



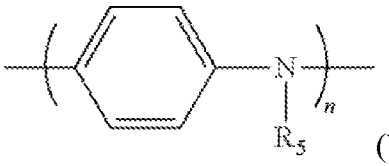
(Va),



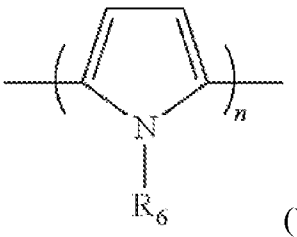
(Vb),



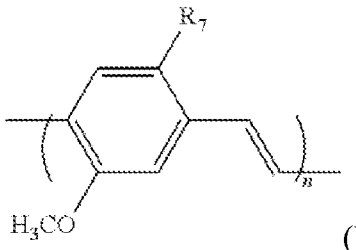
(Vc),



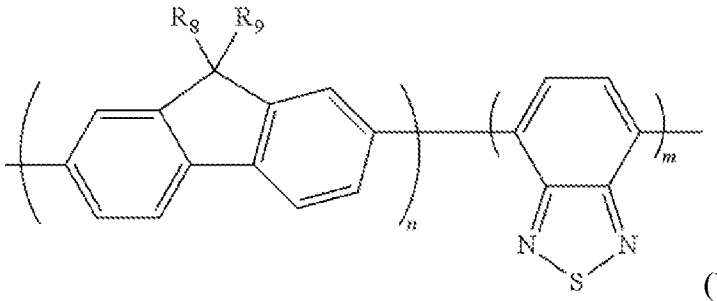
(Vd),



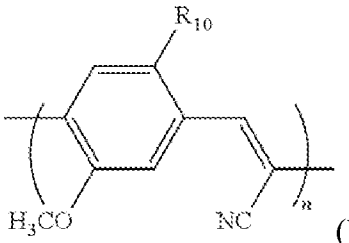
(Ve),



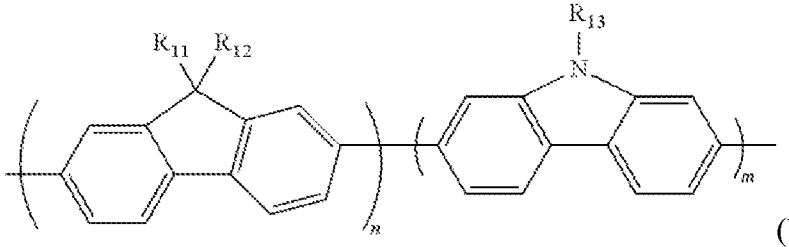
(Vf),



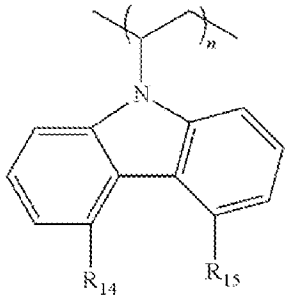
(Vg),



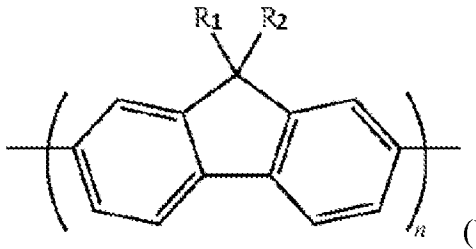
(Vh),



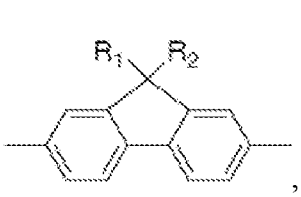
(Vi), or

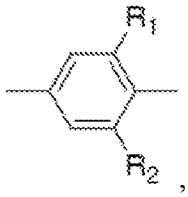


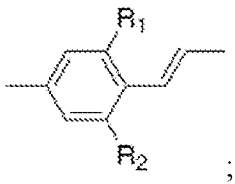
(Vj); wherein R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, R_{10}, R_{11}, R_{12}, R_{13}, R_{14}, and R_{15} are each independently an alkyl chain or oligo ethyleoxide chain or alkyloxide chain of any length between 1-10000 carbon atoms.

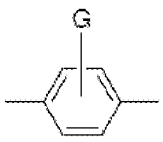
5. The method of claim 4, wherein the conductive polymer has the following chemical structure:  (Va); wherein R_1 and R_2 are each independently an alkyl chain or oligo ethyleoxide chain or alkyloxide chain of any length between 1-10000 carbon atoms.

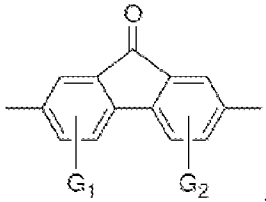
6. An electrically conductive polymer or conductive polymer not soluble in an alcohol-water solvent or water formed by heating or thermally treating a polymer an having the following chemical structure: —A_n—E_m—F_q— (I); wherein A is

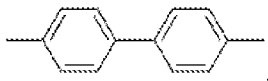


, 

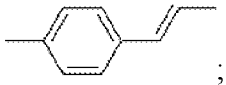
, or 

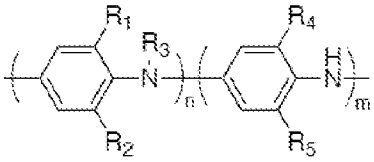
; E and F are each independently 

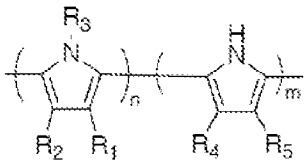
, 

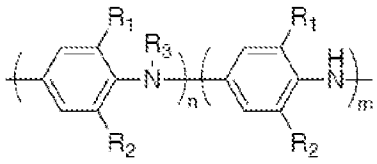
, 

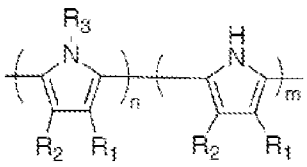
, or

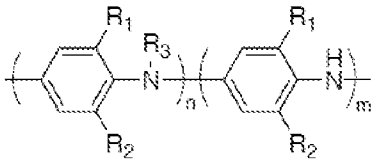

; R_1 and R_2 are each independently an alkyl chain or oligo ethyleoxide chain or alkyloxide chain of any length between 1-10000 carbon atoms; G and G_1 are each independently —H, —F, —$COOCH_3$, —COOH, or —SO_3CH_3; n + m + q = 1, and representing the relative abundance in the polymer chain; n, m, and q are each independently any number between 0-1; and, R_1 and R_2 are each independently hydroxide terminated or carboxylic acid or carboxylate salt terminated; —Q_n—Q'_m— (II); wherein Q and Q' are each independently is one of the following chemical structures:

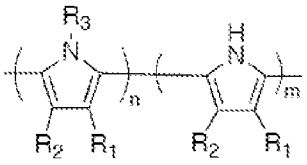


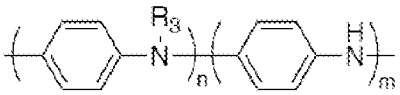


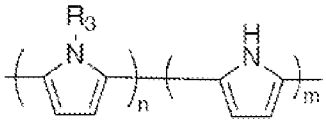


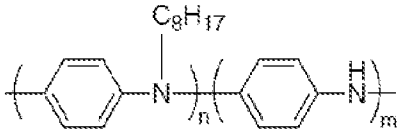


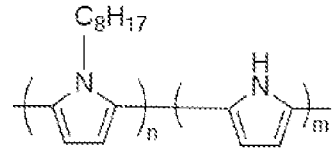


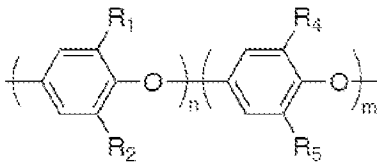


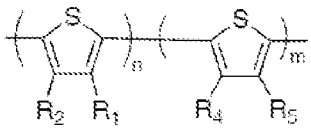


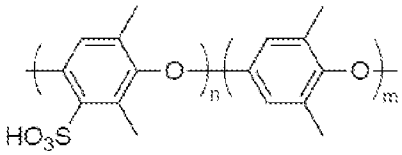




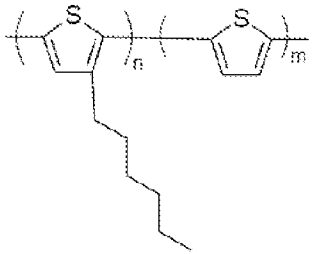


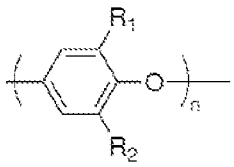


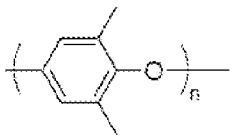


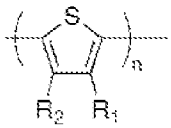


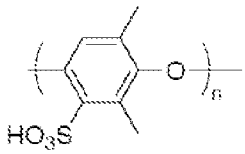
Or Li, Na, K salts



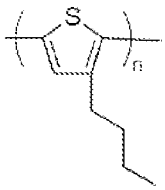


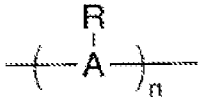
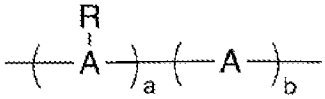


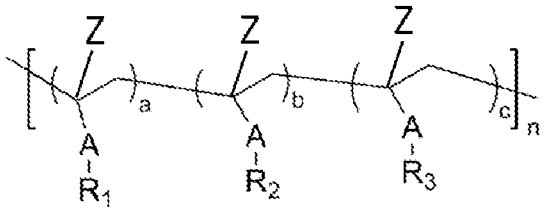




Or Li, Na, K salts

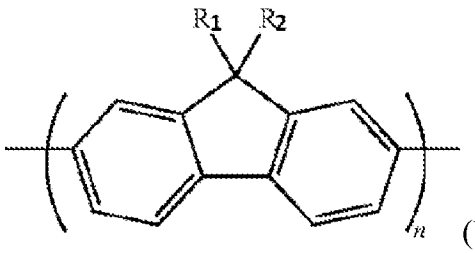


; n is between 1 and 100M; R_1 and R_2 are each independently an alkyl chain or oligo ethyleoxide chain or alkyloxide chain of any length between 1-10000 carbon atoms; and R_1 and/or R_2 can be hydroxide terminated or carboxylic acid or carboxylate salt terminated;  (III) or  (IIIa);

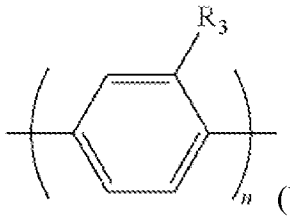


(V); wherein A is —COO—, —O—, —NH—, —S—, or a covalent bond; Z is —H or —CH_3; or, $(X)_n$ (V), wherein X is a conjugated homo polymer, a conjugated copolymer, or a linear polymer with conducting conjugated pending group; wherein the heating or thermally treating the polymer to a temperature that decomposes or removes part or all side chains of the polymer.

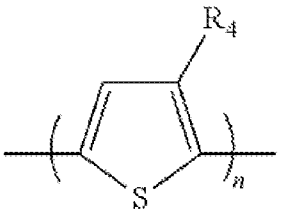
7. The electrically conductive polymer or conductive polymer of claim 6, wherein the polymer has the following chemical structure:



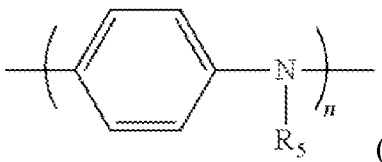
(Va),



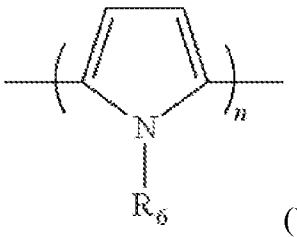
(Vb),



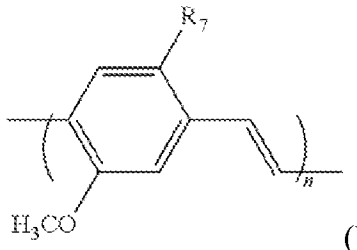
(Vc),



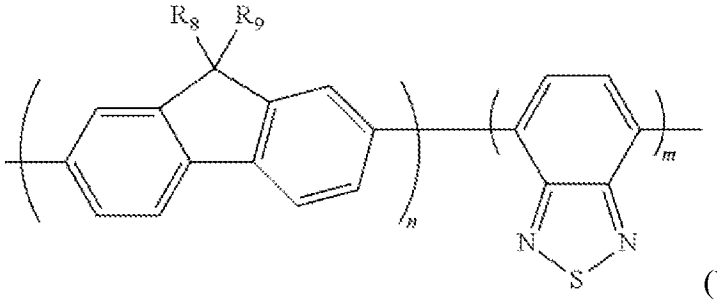
(Vd),



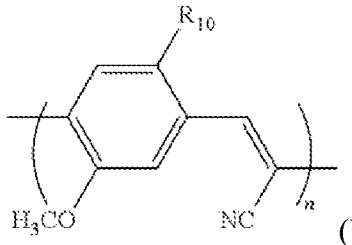
(Ve),



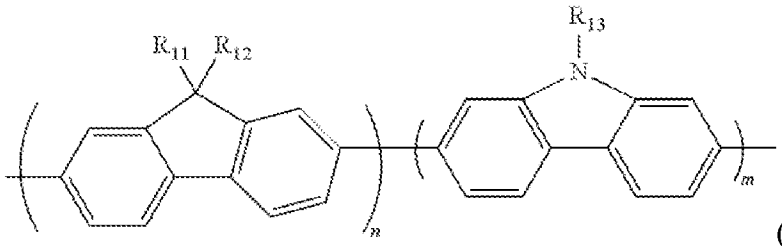
(Vf),



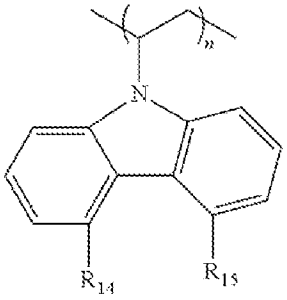
(Vg),



(Vh),

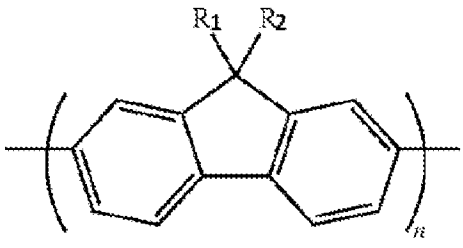


(Vi), or



(Vj); wherein R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, R_{10}, R_{11}, R_{12}, R_{13}, R_{14}, and R_{15} are each independently an alkyl chain or oligo ethyleoxide chain or alkyloxide chain of any length between 1-10000 carbon atoms.

8. The method of claim 6, wherein the polymer has the following chemical structure:

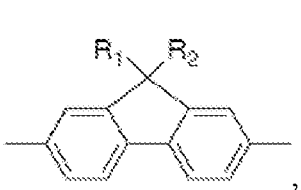
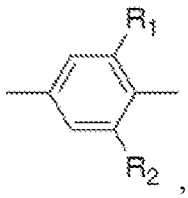
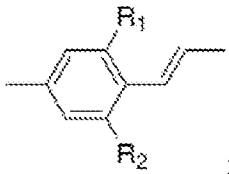
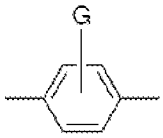
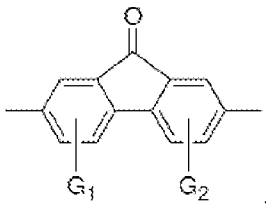
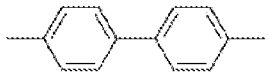
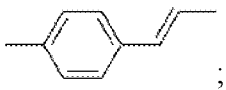


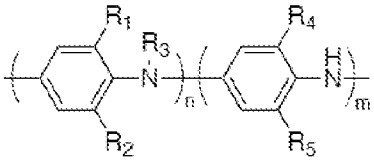
(Va); wherein R_1 and R_2 are each independently an alkyl chain or oligo ethyleoxide chain or alkyloxide chain of any length between 1-10000 carbon atoms.

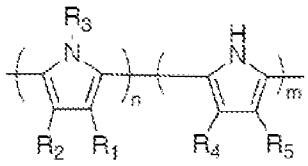
9. A method for applying an electrically conductive polymer to a surface, comprising: (a) removing impurities from a used or spent graphite to produce a washed or regenerated graphite; (b) coating the washed or regenerated graphite with an electrically conductive polymer that is soluble in an alcohol-water solvent or water to produce a coated graphite, wherein the electrically conductive polymer, or one or more monomer units of the polymer, comprises one or more chains, wherein each chain comprises one or more ether, methoxy and/or ethoxy groups, wherein there are

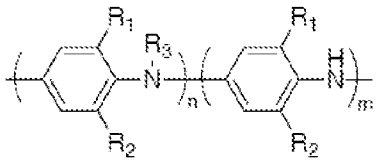
sufficient ether, methoxy and/or ethoxy groups thereby the electrically conductive polymer is soluble in the alcohol-water solvent or water; (c) drying the coated graphite to remove or evaporate part or all of the alcohol and water; and (d) heating or thermally treating the dried coated graphite to a temperature that decomposes or removes part or all side chains of the electrically conductive polymer or conductive polymer.

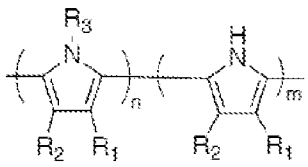
10. The method of claim 9, wherein the electrically conductive polymer or conductive polymer resulting from step (g) is not soluble in the alcohol-water solvent or water.

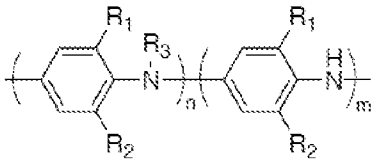
11. The method of claim 10, wherein the electrically conductive polymer or conductive polymer has the following chemical structure: —A_n—E_m—F_q— (I); wherein A is  ,  , or  ; E and F are each independently  ,  ,  , or  ; R_1 and R_2 are each independently an alkyl chain or oligo ethyleoxide chain or alkyloxide chain of any length between 1-10000 carbon atoms; G and G_1 are each independently —H, —F, —$COOCH_3$, —COOH, or —SO_3CH_3; n + m + q = 1, and representing the relative abundance in the polymer chain; n, m, and q are each independently any number between 0-1; and, R_1 and R_2 are each independently hydroxide terminated or carboxylic acid or carboxylate salt terminated; —Q_n—Q'_m— (II); wherein Q and Q' are each independently is one of the following chemical structures:

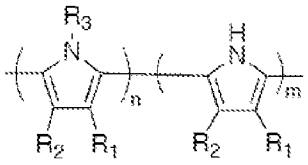


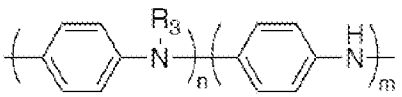


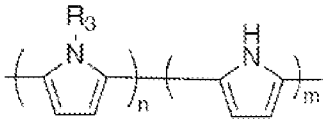


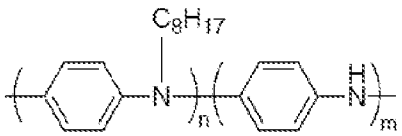


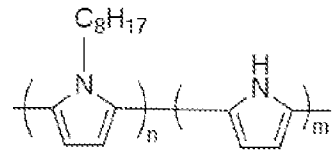


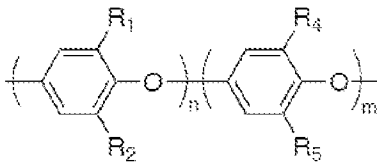


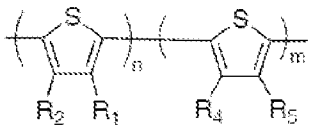


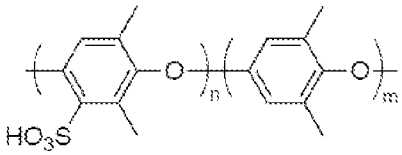




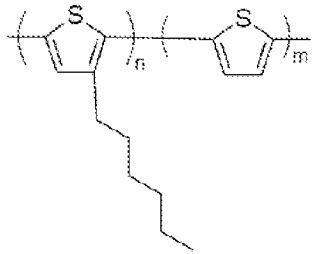


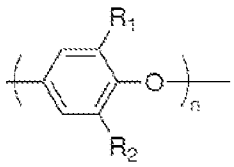


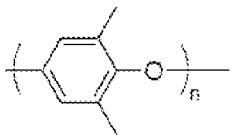


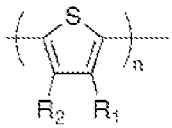


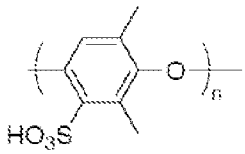
Or Li, Na, K salts



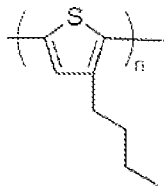


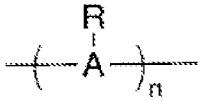
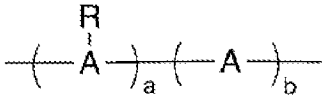


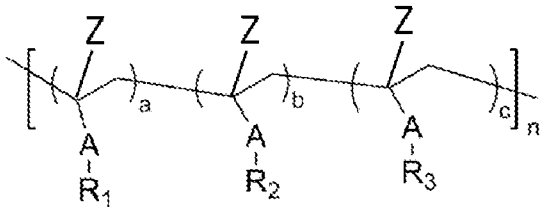




Or Li, Na, K salts

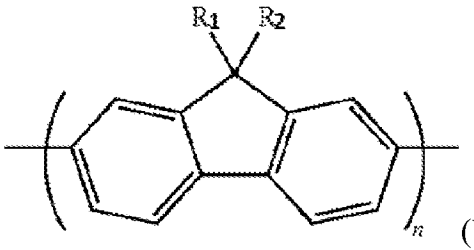


; n is between 1 and 100M; R_1 and R_2 are each independently an alkyl chain or oligo ethyleoxide chain or alkyloxide chain of any length between 1-10000 carbon atoms; and R_1 and/or R_2 can be hydroxide terminated or carboxylic acid or carboxylate salt terminated;  (III) or  (IIIa);

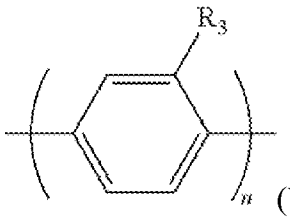


(V); wherein A is —COO—, —O—, —NH—, —S—, or a covalent bond; Z is —H or —CH_3; or, $(X)_n$ (V), wherein X is a conjugated homo polymer, a conjugated copolymer, or a linear polymer with conducting conjugated pending group.

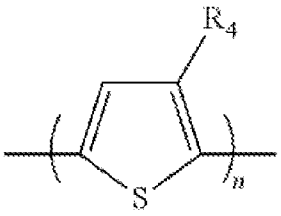
12. The method of claim 11, wherein the conductive polymer has the following chemical structure:



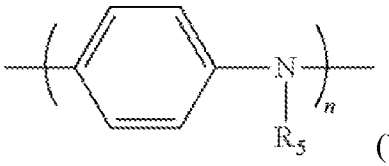
(Va),



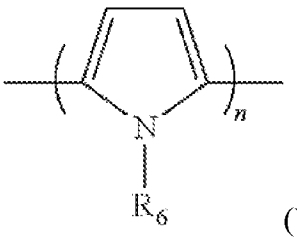
(Vb),



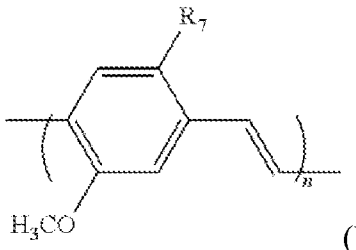
(Vc),



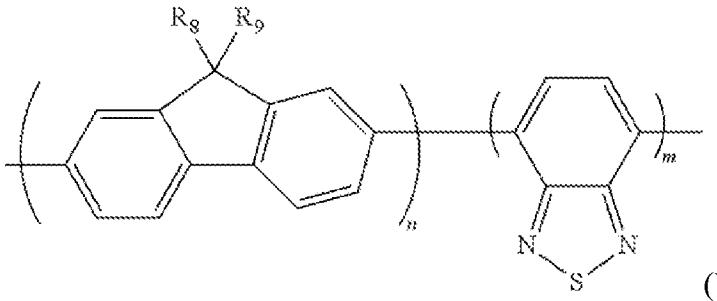
(Vd),



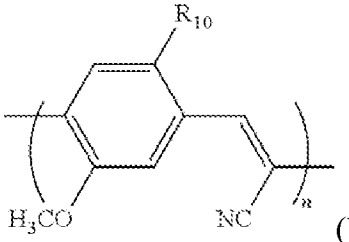
(Ve),



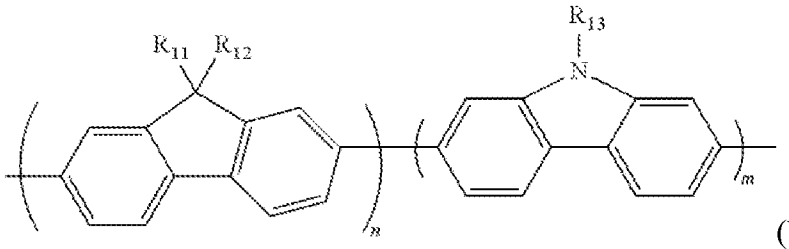
(Vf),



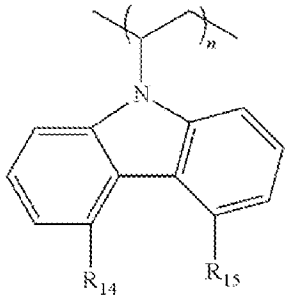
(Vg),



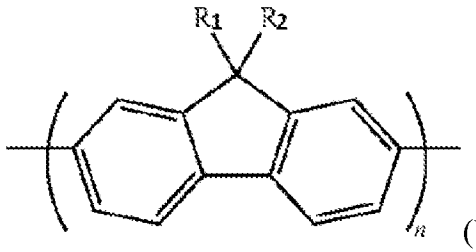
(Vh),



(Vi), or



(Vj); wherein R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, R_{10}, R_{11}, R_{12}, R_{13}, R_{14}, and R_{15} are each independently an alkyl chain or oligo ethyleoxide chain or alkyloxide chain of any length between 1-10000 carbon atoms.

13. The method of claim 12, wherein the conductive polymer has the following chemical structure:  (Va); wherein R_1 and R_2 are each independently an alkyl chain or oligo ethyleoxide chain or alkyloxide chain of any length between 1-10000 carbon atoms.

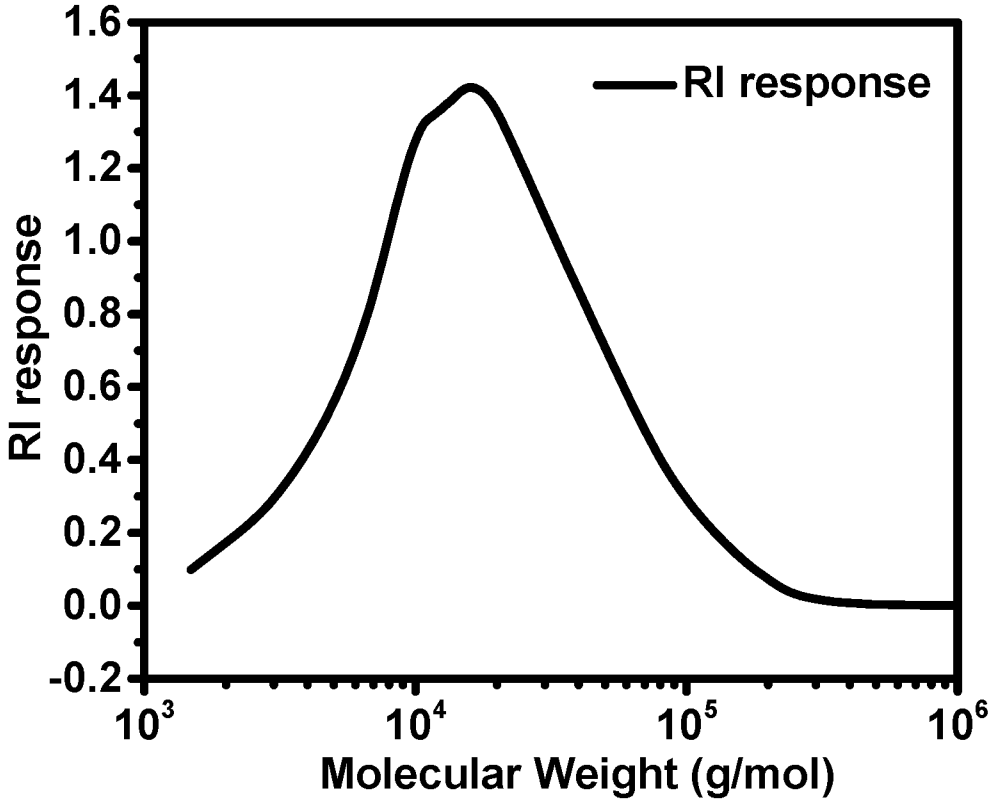


FIG. 1

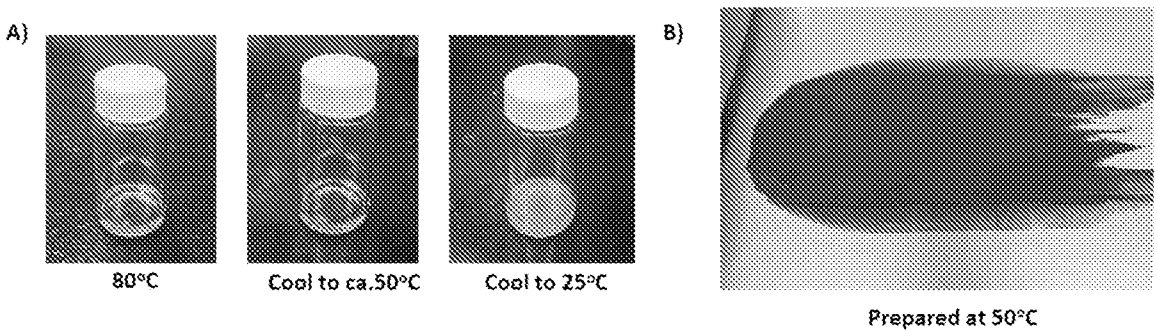


FIG. 2

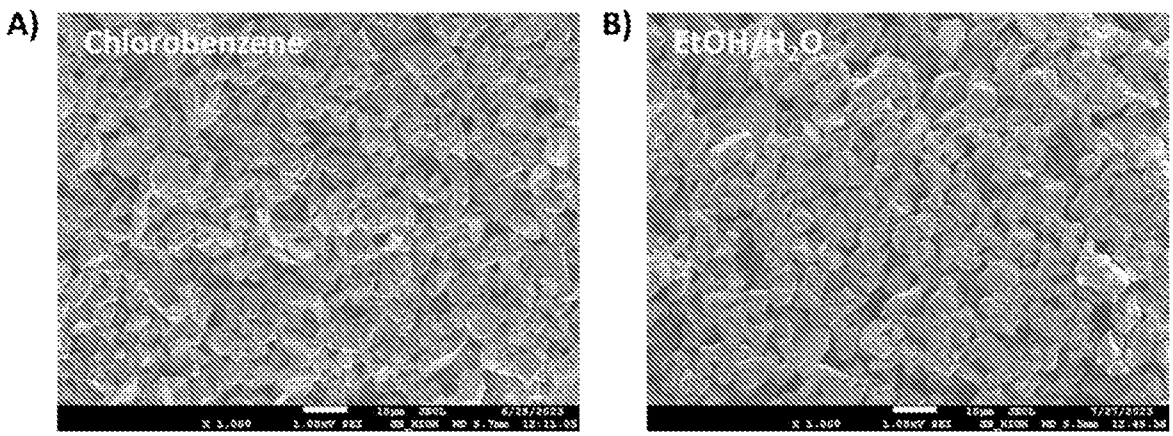


FIG. 3

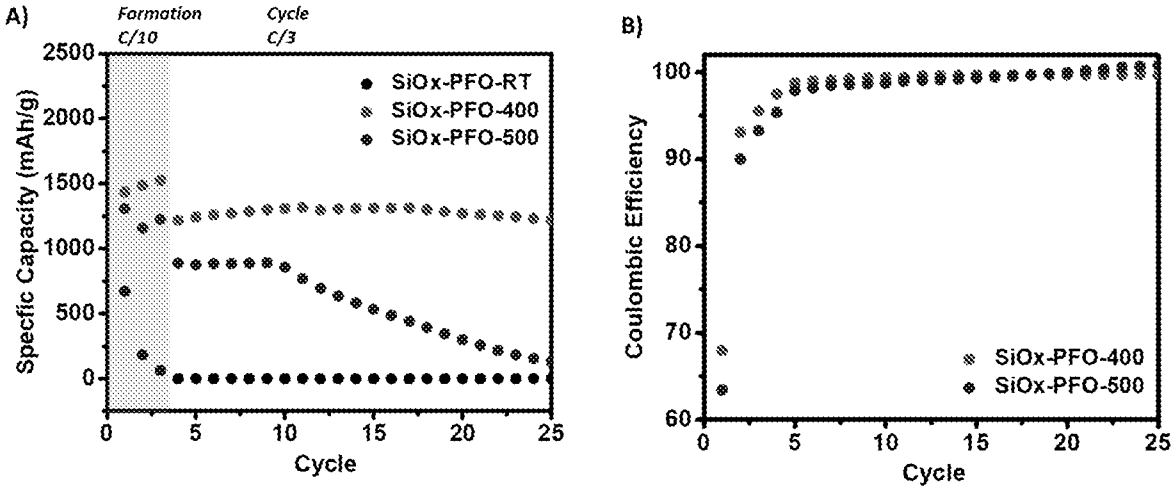

A)
Formation
C/10
Cycle
C/3
Specfic Capacity (mAh/g)
Cycle
SiOx-PFO-RT
SiOx-PFO-400
SiOx-PFO-500
B)
Coulombic Efficiency
Cycle
SiOx-PFO-400
SiOx-PFO-500

FIG. 4

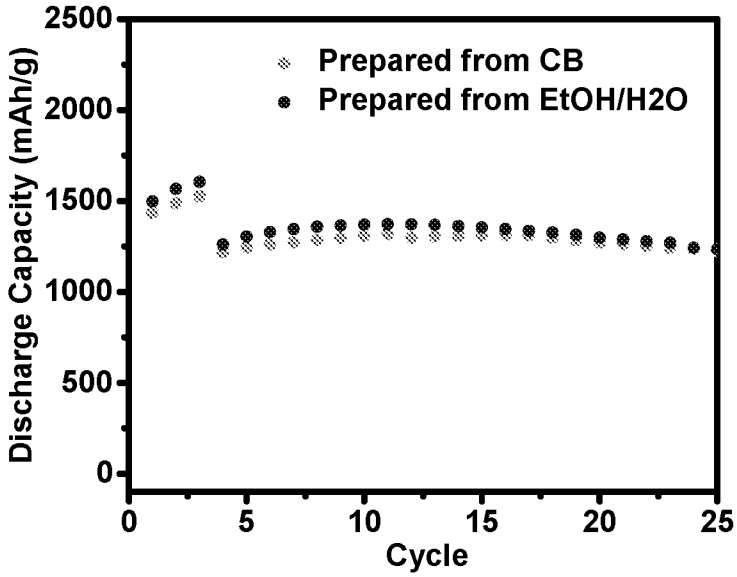

Discharge Capacity (mAh/g)
Cycle
Prepared from CB
Prepared from EtOH/H2O

FIG. 5

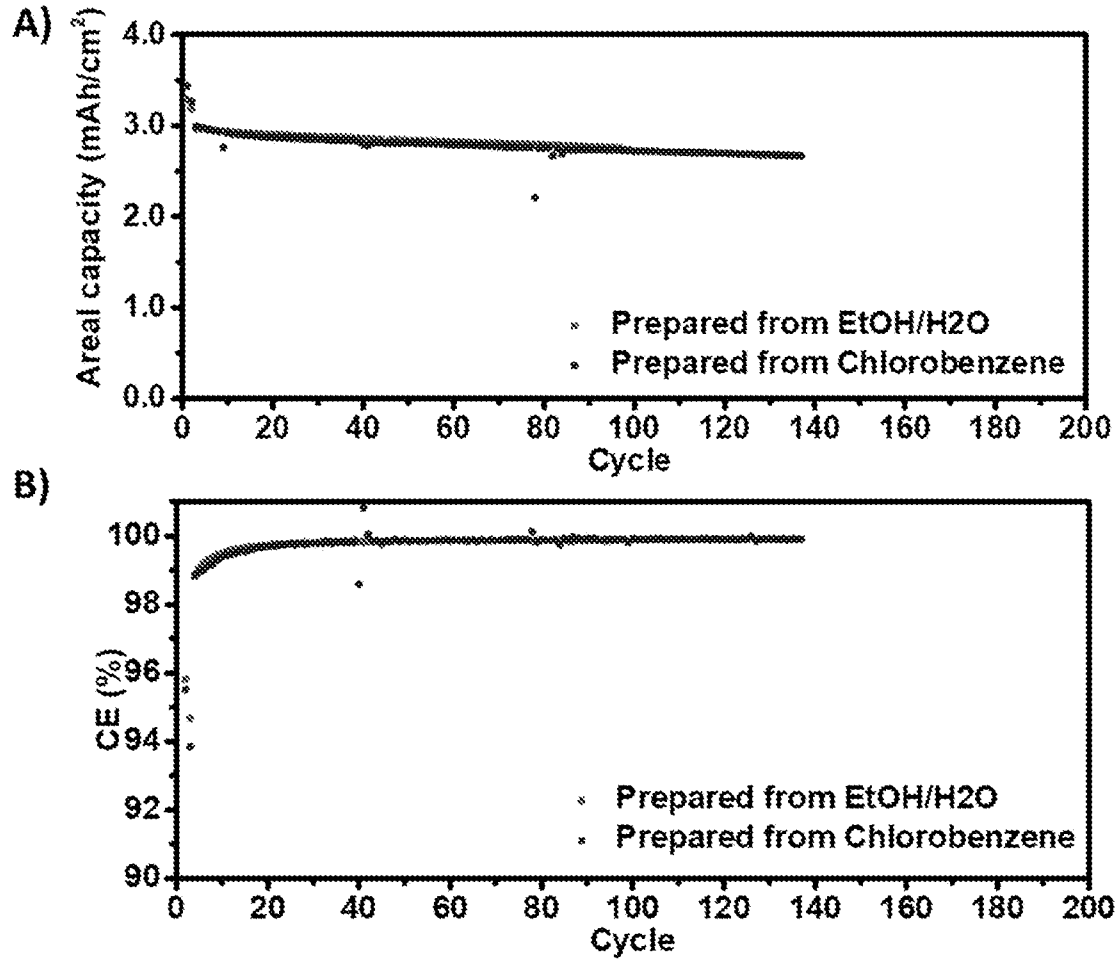

A)
Areal capacity (mAh/cm²)
4.0
3.0
2.0
1.0
0.0
0
20
40
60
80
100
120
140
160
180
200
Cycle
Prepared from EtOH/H2O
Prepared from Chlorobenzene
B)
CE (%)
100
98
96
94
92
90
0
20
40
60
80
100
120
140
160
180
200
Cycle
Prepared from EtOH/H2O
Prepared from Chlorobenzene

FIG. 6

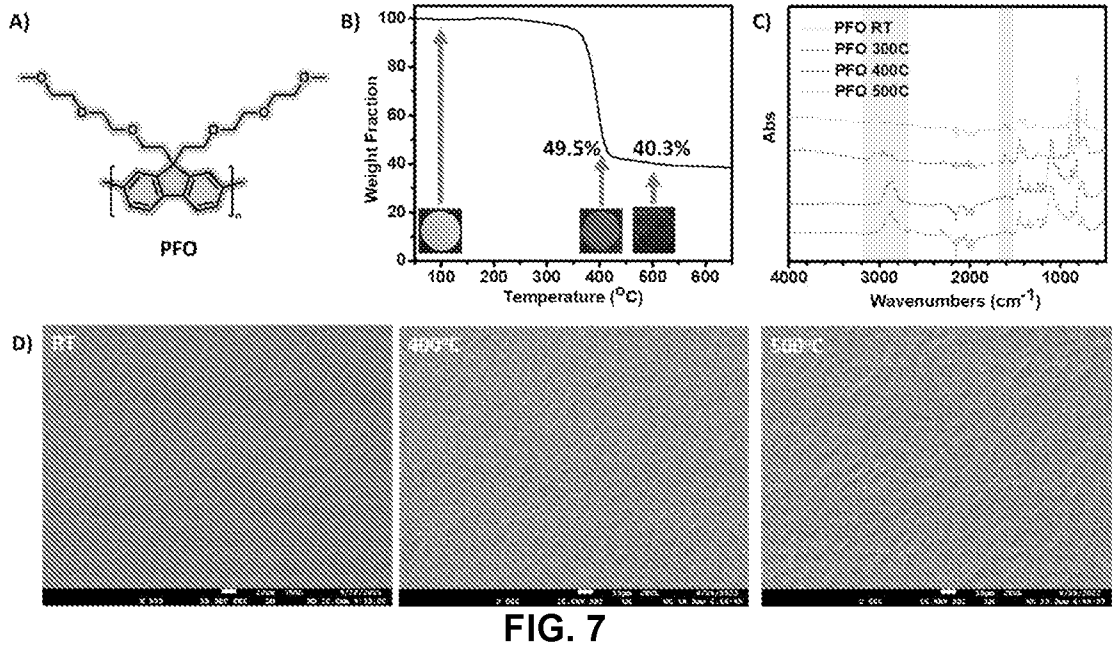

A)
PFO
B)
Weight Fraction
100
80
60
40
20
0
49.5%
40.3%
100
200
300
400
500
600
Temperature (°C)
C)
PFO RT
PFO 300C
PFO 400C
PFO 500C
Abs
4000
3000
2000
1000
Wavenumbers (cm⁻¹)
D)
RT
400°C
500°C

FIG. 7

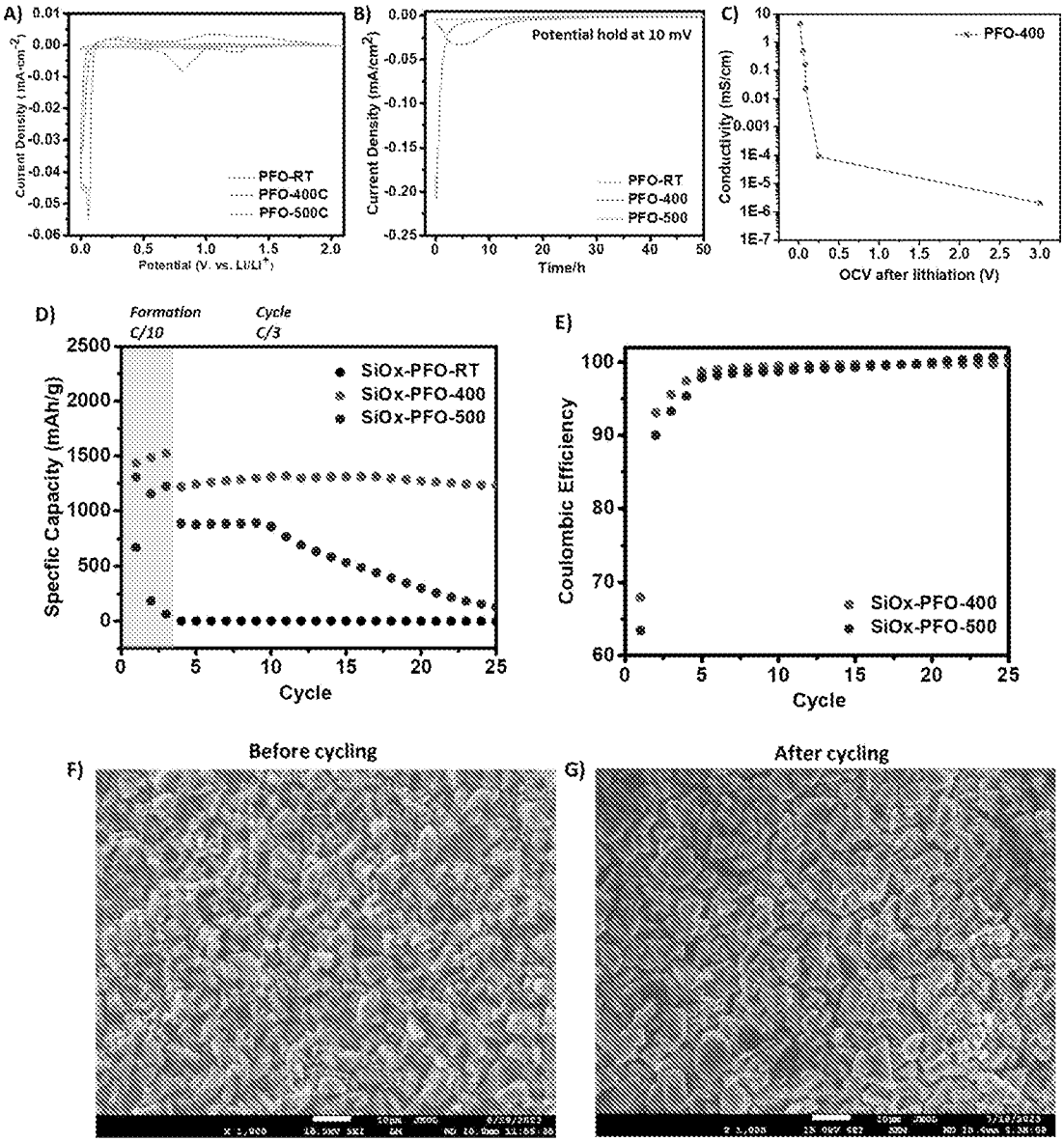

A)
Current Density (mA·cm⁻²)
Potential (V. vs. Li/Li⁺)
PFO-RT
PFO-400C
PFO-500C
B)
Current Density (mA/cm²)
Potential hold at 10 mV
Time/h
PFO-RT
PFO-400
PFO-500
C)
Conductivity (mS/cm)
OCV after lithiation (V)
PFO-400
D)
Formation C/10
Cycle C/3
Specfic Capacity (mAh/g)
Cycle
SiOx-PFO-RT
SiOx-PFO-400
SiOx-PFO-500
E)
Coulombic Efficiency
Cycle
SiOx-PFO-400
SiOx-PFO-500
F)
Before cycling
G)
After cycling

FIG. 8

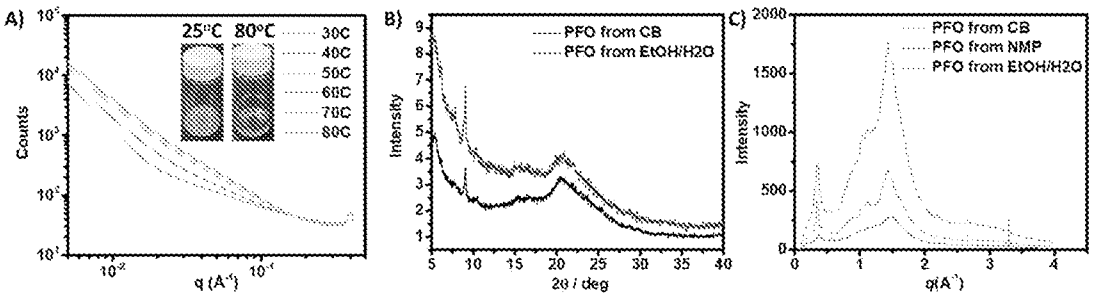

A)
Counts
q (A⁻¹)
25°C
80°C
30C
40C
50C
60C
70C
80C
B)
Intensity
2θ / deg
PFO from CB
PFO from EtOH/H2O
C)
Intensity
q(A⁻¹)
PFO from CB
PFO from NMP
PFO from EtOH/H2O

FIG. 9

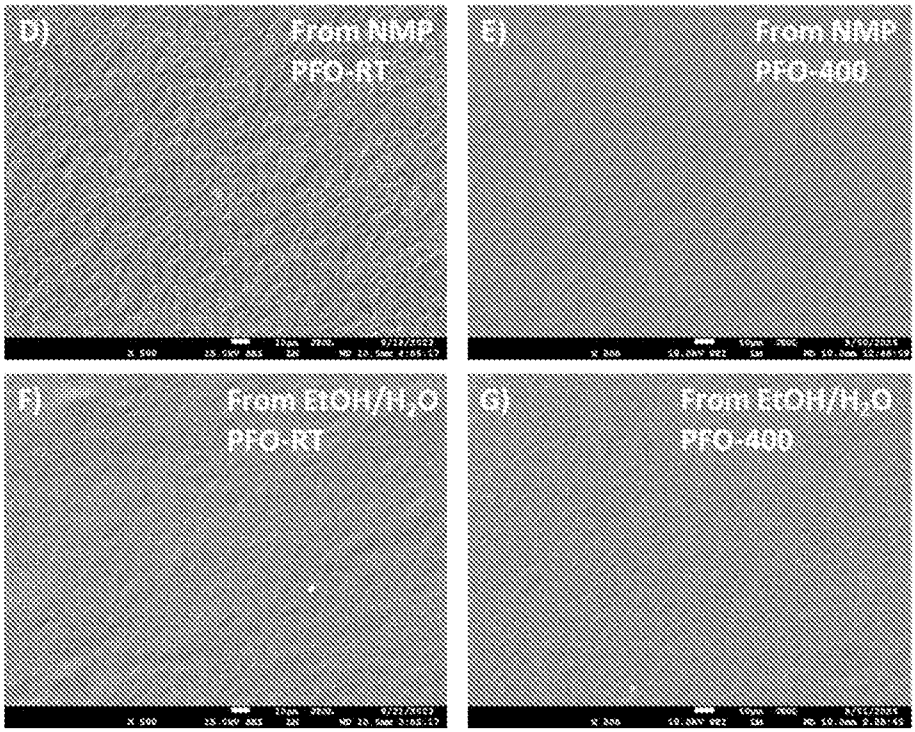


FIG. 9 cont'd

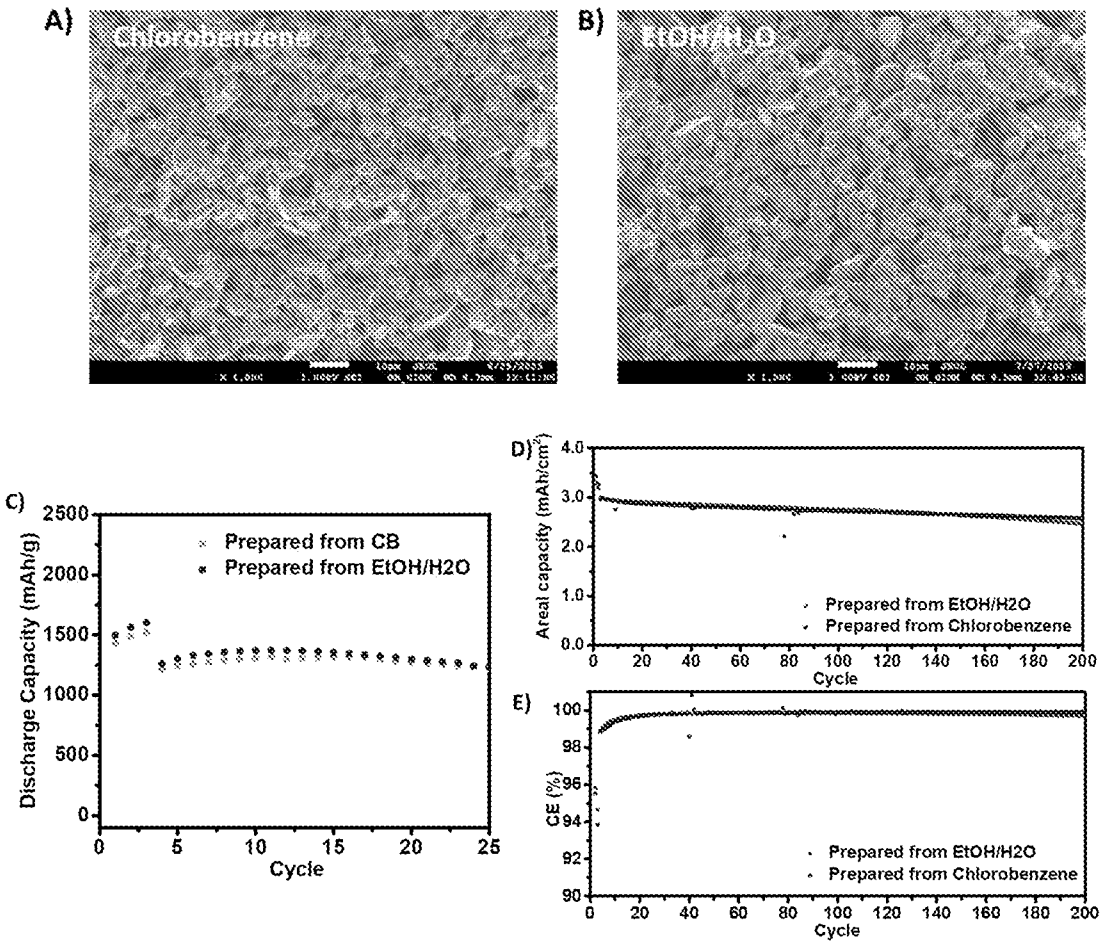


FIG. 10

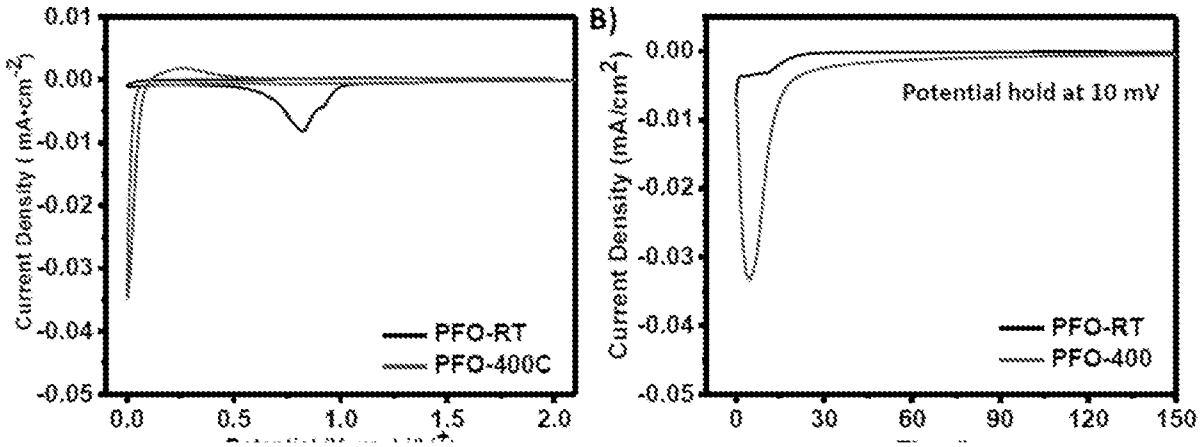

B)
Current Density (mA•cm^{-2})
0.01
0.00
-0.01
-0.02
-0.03
-0.04
-0.05
0.0
0.5
1.0
1.5
2.0
PFO-RT
PFO-400C
Current Density (mA/cm^2)
0.00
-0.01
-0.02
-0.03
-0.04
-0.05
Potential hold at 10 mV
0
30
60
90
120
150
PFO-RT
PFO-400

FIG. 11

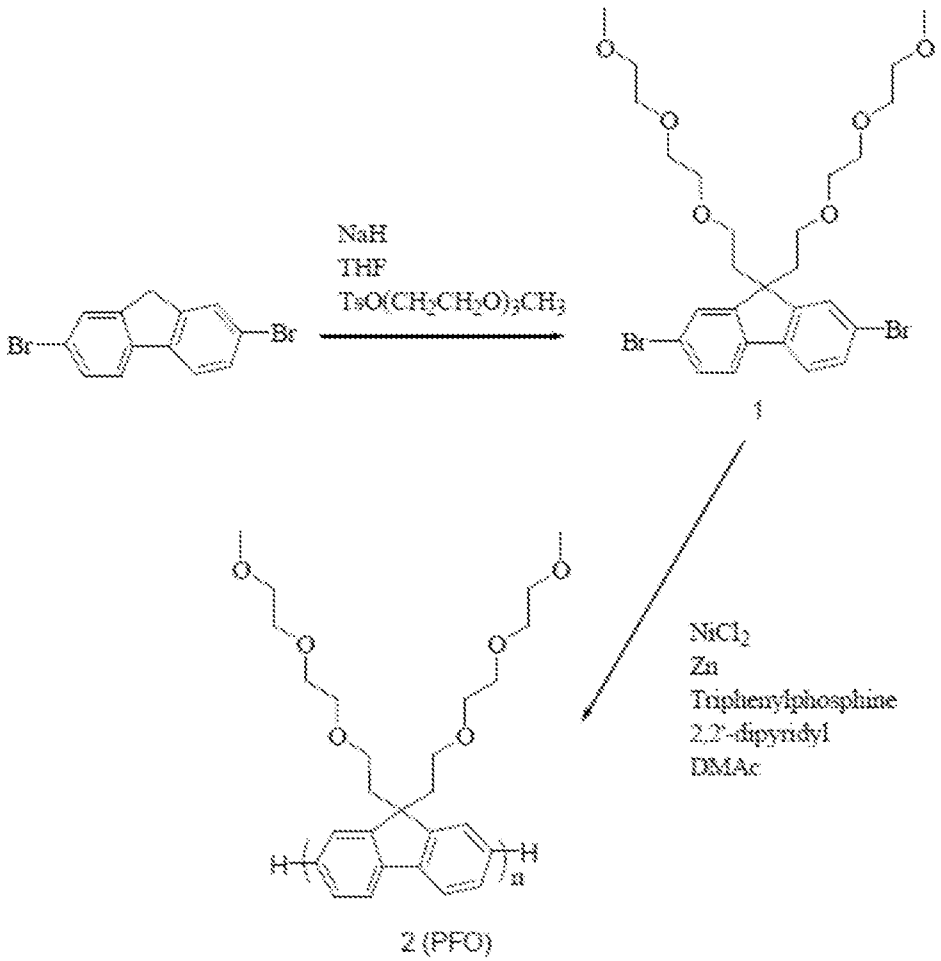

NaH
THF
TsO(CH2CH2O)3CH3
Br
Br
1
NiCl2
Zn
Triphenylphosphine
2,2'-dipyridyl
DMAc
2 (PFO)

FIG. 12

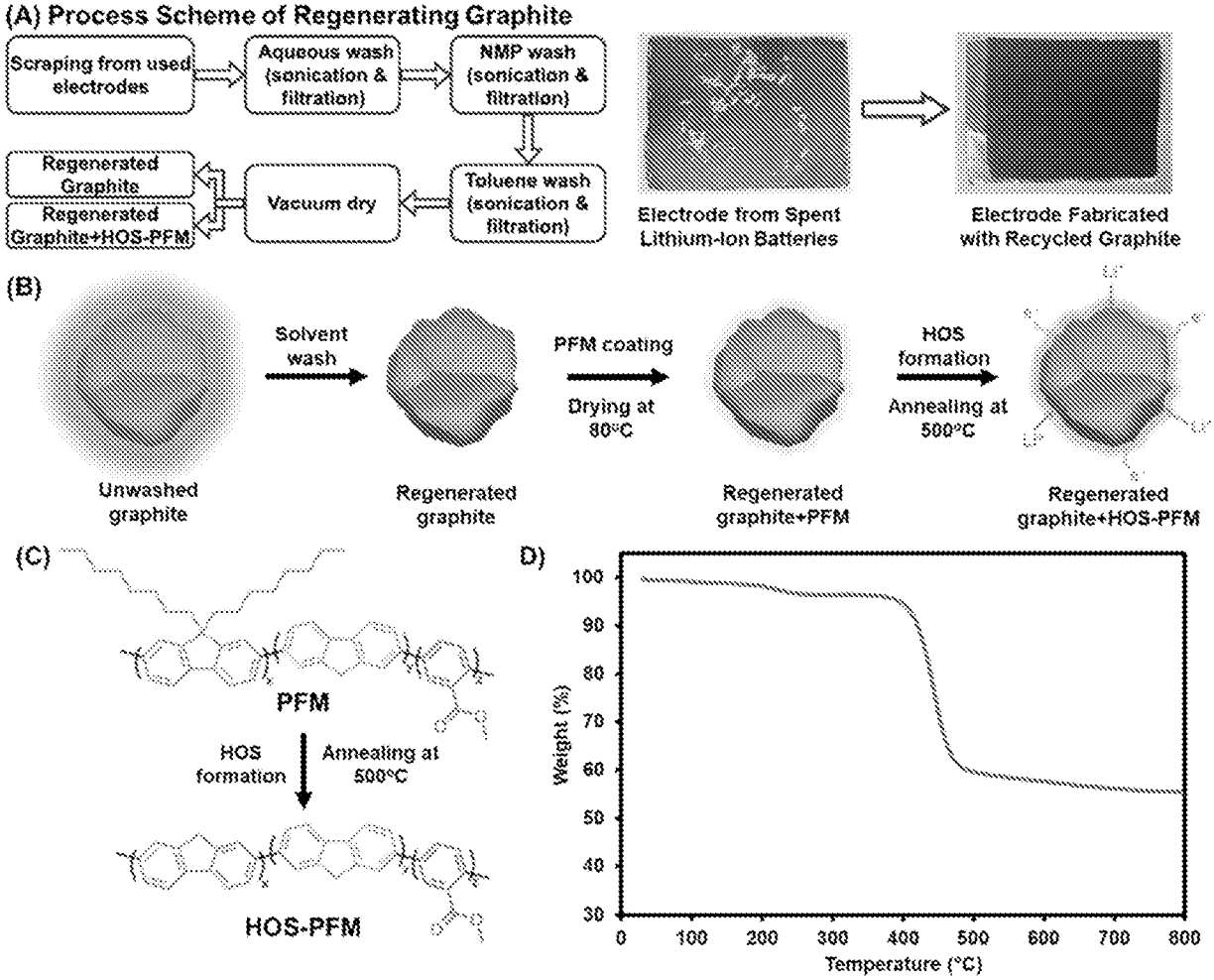

(A) Process Scheme of Regenerating Graphite
Scraping from used electrodes
Aqueous wash (sonication & filtration)
NMP wash (sonication & filtration)
Toluene wash (sonication & filtration)
Vacuum dry
Regenerated Graphite
Regenerated Graphite+HOS-PFM
Electrode from Spent Lithium-Ion Batteries
Electrode Fabricated with Recycled Graphite
(B)
Solvent wash
PFM coating
Drying at 80°C
HOS formation
Annealing at 500°C
Unwashed graphite
Regenerated graphite
Regenerated graphite+PFM
Regenerated graphite+HOS-PFM
(C)
PFM
HOS formation
Annealing at 500°C
HOS-PFM
D)
Weight (%)
Temperature (°C)

FIG. 13

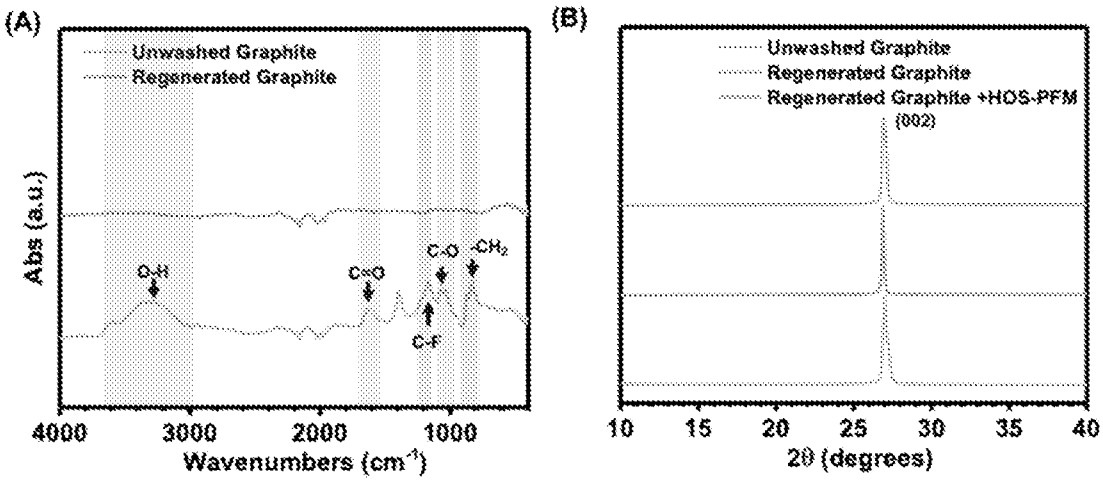

(A)
Unwashed Graphite
Regenerated Graphite
Abs (a.u.)
O-H
C=O
C-O
-CH2
C-F
Wavenumbers (cm-1)
(B)
Unwashed Graphite
Regenerated Graphite
Regenerated Graphite +HOS-PFM
(002)
2θ (degrees)

FIG. 14

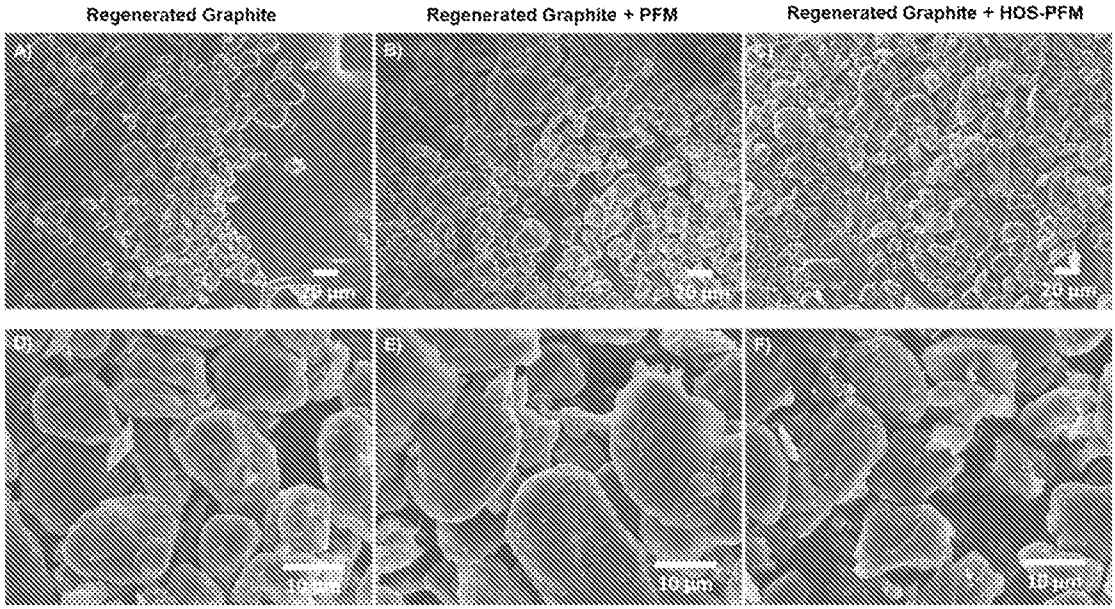

Regenerated Graphite
Regenerated Graphite + PFM
Regenerated Graphite + HOS-PFM
A1
B1
C1
A2
B2
C2
50 μm
50 μm
50 μm
10 μm
10 μm
10 μm

FIG. 15

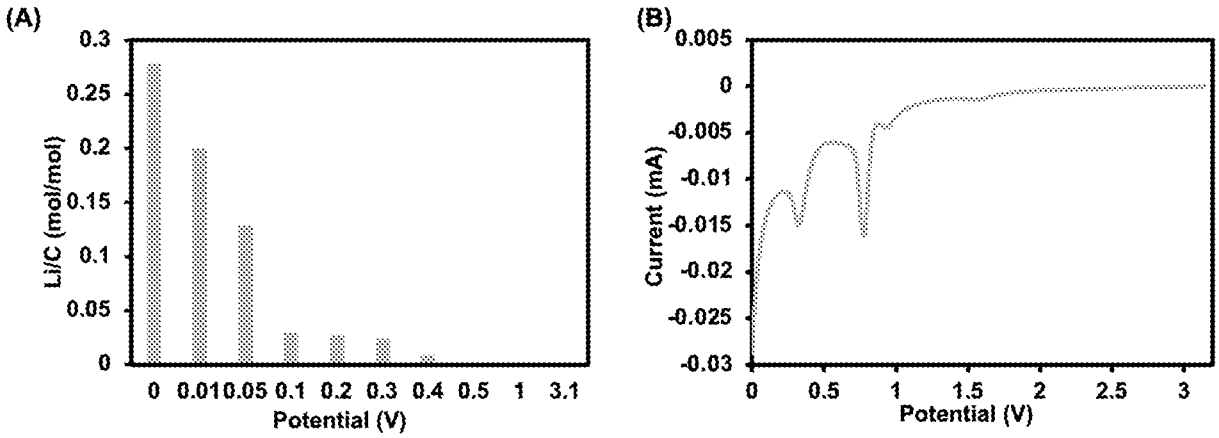

(A)
Li/C (mol/mol)
0.3
0.25
0.2
0.15
0.1
0.05
0
0 0.01 0.05 0.1 0.2 0.3 0.4 0.5 1 3.1
Potential (V)
(B)
Current (mA)
0.005
0
-0.005
-0.01
-0.015
-0.02
-0.025
-0.03
0 0.5 1 1.5 2 2.5 3
Potential (V)

FIG. 16

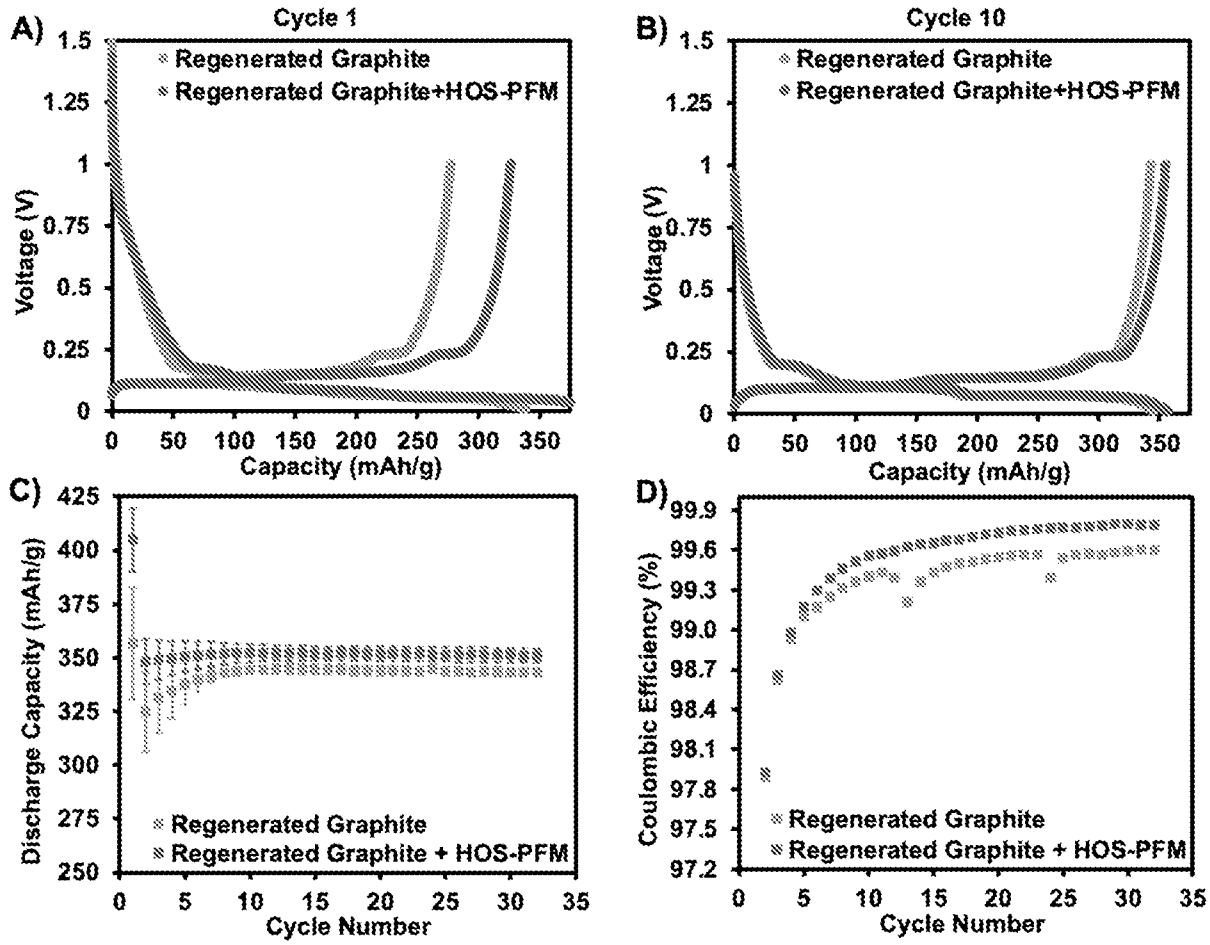

A)
Cycle 1
Regenerated Graphite
Regenerated Graphite+HOS-PFM
Voltage (V)
Capacity (mAh/g)
B)
Cycle 10
Regenerated Graphite
Regenerated Graphite+HOS-PFM
Voltage (V)
Capacity (mAh/g)
C)
Discharge Capacity (mAh/g)
Regenerated Graphite
Regenerated Graphite + HOS-PFM
Cycle Number
D)
Coulombic Efficiency (%)
Regenerated Graphite
Regenerated Graphite + HOS-PFM
Cycle Number

FIG. 17

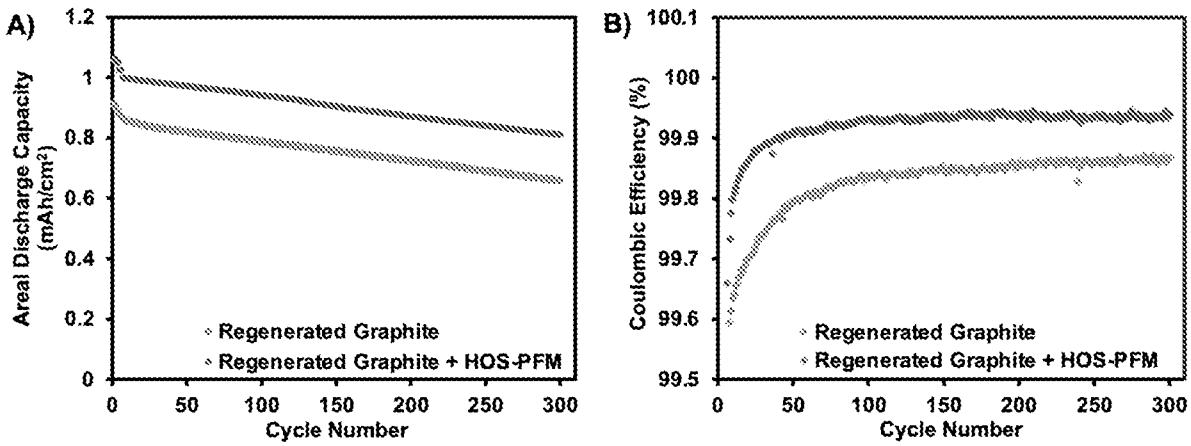

A)
Areal Discharge Capacity (mAh/cm²)
Regenerated Graphite
Regenerated Graphite + HOS-PFM
Cycle Number
B)
Coulombic Efficiency (%)
Regenerated Graphite
Regenerated Graphite + HOS-PFM
Cycle Number

FIG. 18

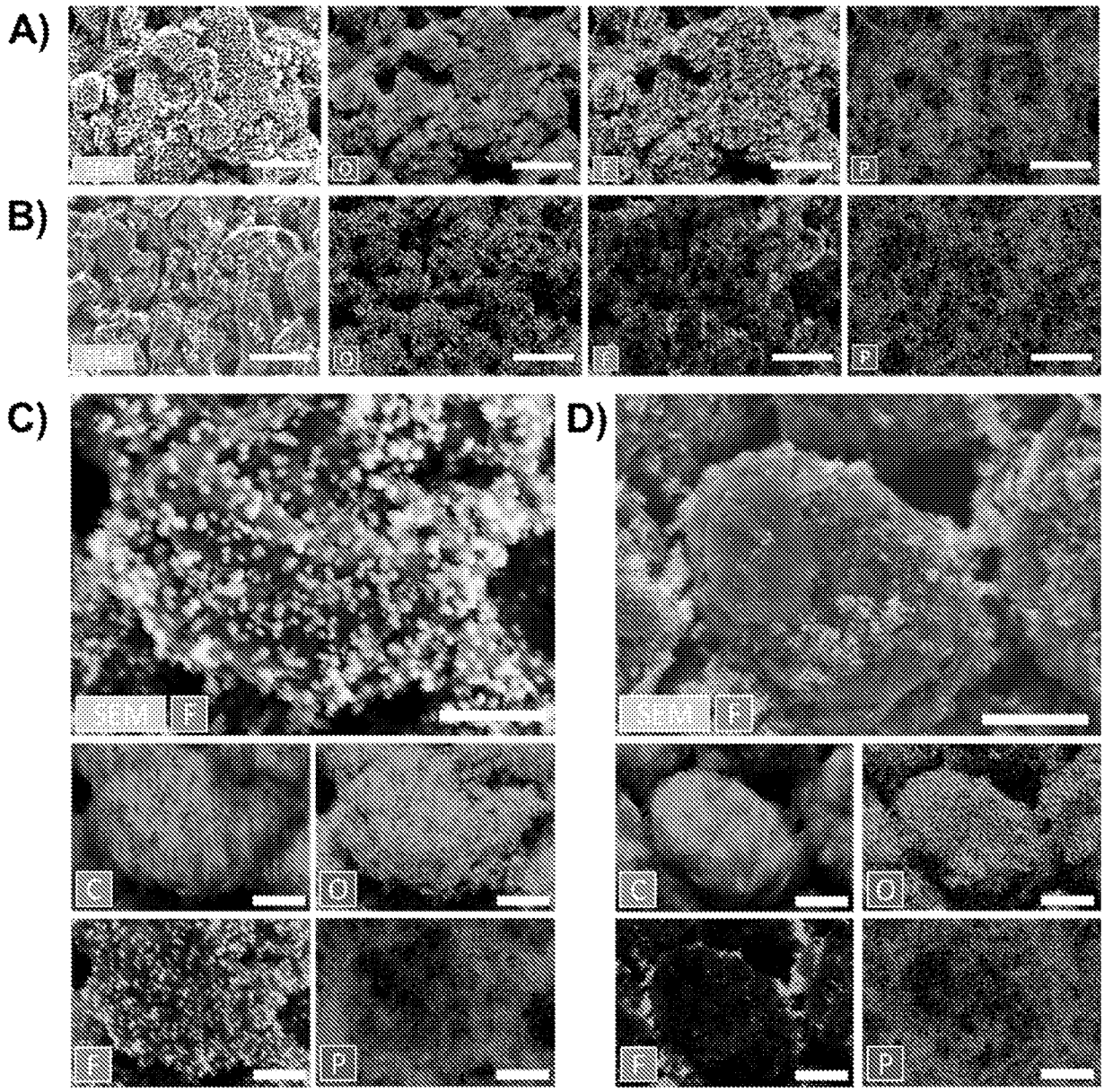


FIG. 19

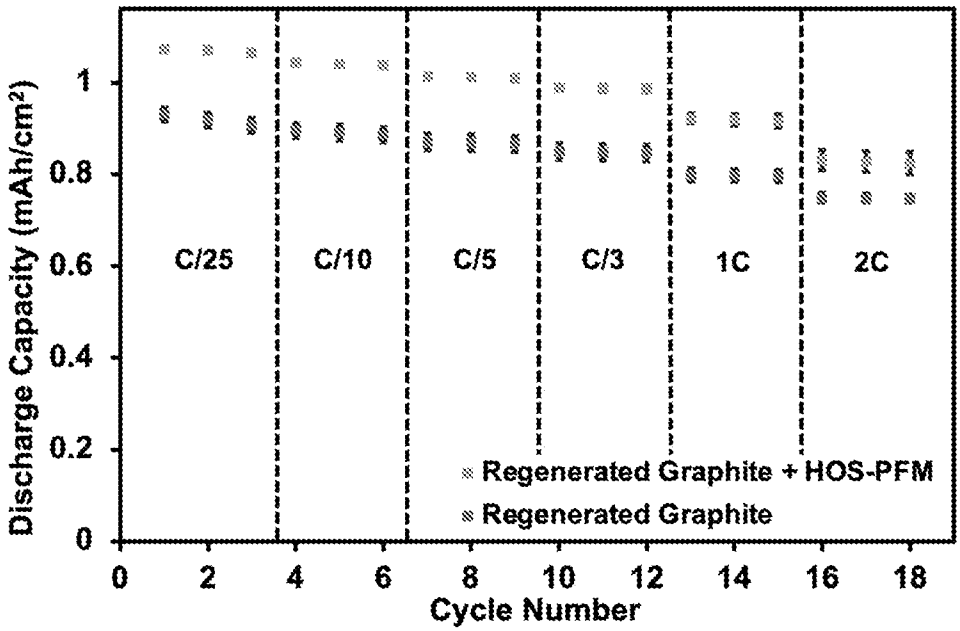

Discharge Capacity (mAh/cm²)
1
0.8
0.6
0.4
0.2
0
C/25
C/10
C/5
C/3
1C
2C
Regenerated Graphite + HOS-PFM
Regenerated Graphite
0
2
4
6
8
10
12
14
16
18
Cycle Number

FIG. 20

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/056284

A. CLASSIFICATION OF SUBJECT MATTER

IPC: ***H01B 1/06*** (2025.01); ***H01B 1/12*** (2025.01); ***C09D 7/65*** (2025.01); *C09D 165/00* (2025.01)

CPC: ***H01B 1/06; H01B 1/12; C09D 7/65;*** *C09D 165/00*

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History Document

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

See Search History Document

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

See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2023/0015653 A1 (SILA NANOTECHNOLOGIES INC) 19 January 2023 (19.01.2023) para [0044]; para [0078]; para [0111]; para [0137]	1-5,9-13
A	US 7,960,037 B2 (LIU et al.) 14 June 2011 (14.06.2011) abstract; col 3, ln 44-57; Fig. 1B	1-5,9-13
A	US 4,880,508 A (ALDISSI et al.) 14 November 1989 (14.11.1989) abstract	1-5,9-13
A	US 9,722,252 B2 (LIU et al.) 01 August 2017 (01.08.2017) col 2, ln 55-57; Fig. 1, formula; Fig. 12, formula	1-5,9-13
A	YAO et al. "A 5 V-class cobalt-free battery cathode with high loading enabled by dry coating", Energy Environ. Sci., February 2023, 16, pp 1620-1630 entire document	1-5,9-13

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 February 2025 (26.02.2025)	**04 March 2025 (04.03.2025)**

Name and mailing address of the ISA/US	Authorized officer
COMMISSIONER FOR PATENTS **MAIL STOP PCT, ATTN: ISA/US** **P.O. Box 1450** **Alexandria, VA 22313-1450** **UNITED STATES OF AMERICA**	**KARI RODRIQUEZ**
Facsimile No. **571-273-8300**	Telephone No. **PCT Help Desk: 571-272-4300**

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/056284

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1.

Group I: Claims 1-5 and 9-13 directed to a method for applying an electrically conductive polymer to a surface.

Group II: Claims 6-8, directed to an electrically conductive polymer or conductive polymer not soluble in an alcohol-water solvent or water formed by heating or thermally treating a polymer an having the following chemical structure: -An-Em-Fq-(I).

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☑ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.: **1-5,9-13**

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.