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(54) Title: HIGH CAPACITY CATHODE FOR USE IN SUPERCAPACITORS AND BATTERIES AND METHODS FOR MAUFACTURING SUCH CATHODES

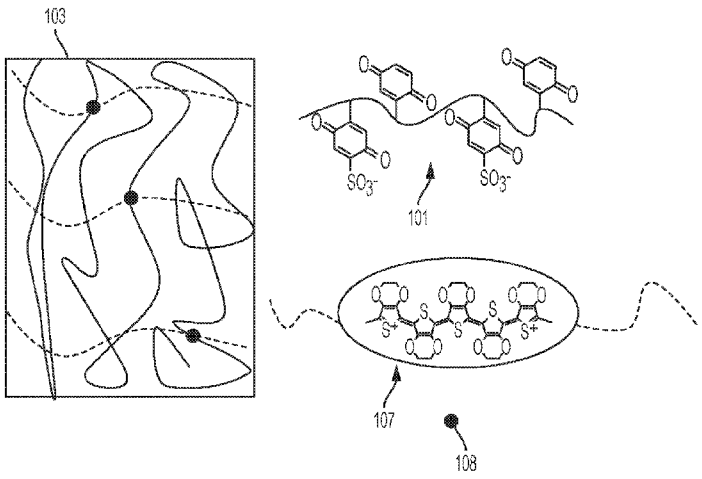

Figure 11

(57) Abstract: Energy storage devices, having a cathode spaced apart from said cathode with an electrolyte in contact with said anode and said cathode, and wherein the cathode has a capacitive polymer comprising an alkane chain backbone with pendant quinone units and a conductive polymer in an interpenetrating network.

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— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

High Capacity Cathode for Use in Supercapacitors and Batteries and Methods for Manufacturing such Cathodes

Related Application Information

[0001] This patent application claims the benefit of U.S. Provisional Application No. 62/175,912, filed on June 15, 2015, the entire content of which is hereby incorporated by reference.

BACKGROUND

1. Technical Field

[0002] The field of the currently claimed embodiments of this invention relate to polymer composite materials, their precursors, and methods of using such materials and precursors.

2. Background

[0003] The fast kinetics of organic-redox active compounds ("ORACs") offer promising benefits in cathodes for energy storage devices, *e.g.* supercapacitors and batteries, as compared to conventional metal cathodes. In particular, conventional transition metal cathodes which use intercalation chemistry have slow kinetics, poor reversibility due to structural changes/cracking, irreversibility issues, and variable volumes. However, several problems must be solved before ORACs may be useful over conventional cathode materials in supercapacitors and batteries.

[0004] For instance, when small molecules, oligomers, or polymers of the class of ORACs are used as organic cathodes, dissolution occurs during charging and discharging resulting in low cycling stability over time. Moreover, the theoretical capacity/energy density of the ORAC is often limited due to structural considerations (*e.g.*, high molecular weight of the polymer backbone, low number of electrons per monomer unit, and high molecular weight of the monomer unit) of the ORAC.

[0005] Another problem to be solved is that the theoretical capacity of organic cathodes cannot often be fully achieved due to insufficient solvent and ion accessibility (low ionic conductivity). Moreover, the ORAC must poses reversible electrochemical properties. Often

ORAC do often not have intrinsically reversible electrochemical behavior which is mandatory to achieve many charge-discharge cycles without capacity loss.

[0006] Furthermore, carbon conductors in cathodes often lack mediator functionality, which contributes to the reversibility of the redox chemistry of the ORAC, and is necessary for a high charging/discharging life cycle. Even still, more challenges still remain, such as the fact that ORACs are usually only soluble in non-ecofriendly solvents, and use of impossible to dissolve carbon conductors (*e.g.*, carbon blacks) result in inhomogeneous slurries which need extensive and costly homogenization procedures.

[0007] Finally, even in the case with ORACs which are known to have high theoretical capacities, these compounds tend to have non-commercially available precursors and require complex multistep syntheses, which results in low yields and high costs.

[0008] Therefore, there remains a need for improved materials, methods of formation/synthesis, and precursors for ORACs in cathodes.

SUMMARY OF THE INVENTION

[0009] Embodiments of the invention provide an energy storage device having a cathode spaced apart from an anode, with an electrolyte in contact with the anode and cathode; wherein the cathode comprises cathode comprises a capacitive polymer and a conductive polymer, the capacitive polymer comprising an alkane chain backbone with pendant quinone units; and where the capacitive polymer and conductive polymer form an interpenetrating network.

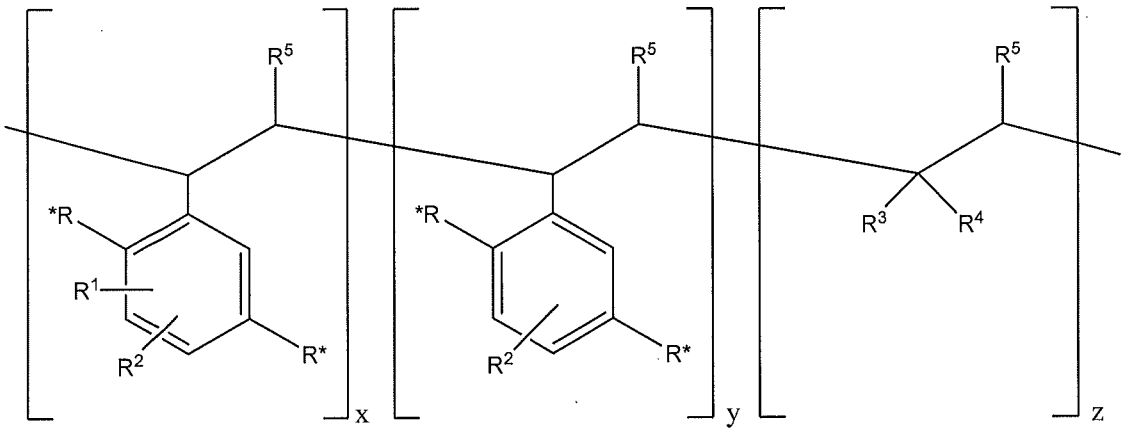
[0010] Embodiments of the invention also provide an electrode comprising a capacitive polymer and conductive polymer, where capacitive polymer comprises an alkane chain backbone with pendant quinone units, and the capacitive polymer and the conductive polymer form an interpenetrating network.

[0011] Embodiments of the invention provide a method of producing an energy storage device, comprising, providing a composition containing a capacitive polymer and a conductive polymer, depositing the composition on a current collector, placing an anode spaced apart from said composition, providing an electrolyte in contact with the composition and the anode. Where

the capacitive polymer comprises an alkane chain backbone with pendant quinone unit; and the capacitive polymer and the conductive polymer form an interpenetrating network.

[0012] Embodiments of the invention provide a method of producing an electrode, comprising, providing a composition containing a capacitive polymer, a conductive polymer, and a solvent; and depositing the composition on a substrate. Where the capacitive polymer comprises an alkane chain backbone with pendant quinone unit, and the capacitive polymer and the conductive polymer form an interpenetrating network.

[0013] Embodiments of the invention provide a polymer of formula (I)

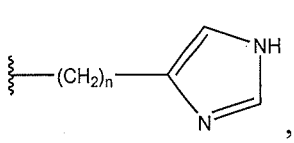


(I)

wherein:

each R*, independently, is OR^a, =O , O-alkyl, $-OCO_2R^4$, -O-silyl group, or a protected hydroxyl group;

each R^1, independently, is $-SO_3R^a$, $-CO_2R^a$, haloalkyl, $-(CH_2)_n-N(R^6)_2$, $-(CH_2)_n-PO_3R^a$,



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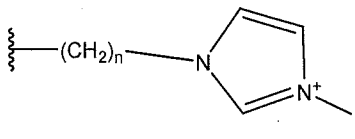
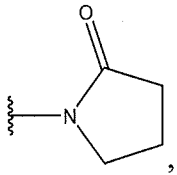
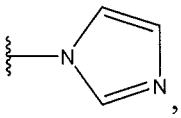
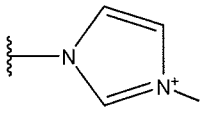


, $-SO_2N(R^5)_2$, $-SO_2R^5$, $-N(SO_2R^6)_2$, $-N(SO_2CF_3)_2$, -CN, halo, or nitro;

each R^2, independently, is H, alkoxy, alkyl, halo, cyano, haloalkyl, or nitro;

each R^3, independently, is alkyl, aryl, $-(CH)_2CO_2R^5$, -OH, $-OC(=O)R^6$, $-C(=O)NHR^5$, $-NHC(=O)CH_3$, $-(CH_2)_mSO_3R^a$, $-(CH_2)_m-PO_3R^a$, $-(CH_2)_mN^+(R^4)_3$,  ,  ,  , $-C(=O)NH-C(CH_3)_2-CH_2SO_3R^a$, $-C(=O)NH(CH_2)_3N^+(CH_3)_2-(CH_2)_3SO_3^-$, or -CN;

each R^4, independently, is H, alkyl, halo, or haloalkyl;

each R^5, independently, is H or alkyl;

each R^6, independently, is alkyl or aryl;

each R^7, independently, is alkyl;

each R^a is H or a cation;

n is 0, 1, 2, 3, or 4;

m is 0, 1, 2, or 3;

x is greater than 0 and no greater than 1;

y is no greater than 1; and

z is from 0 to 0.5;

wherein x + y + z = 1, provided that x and z are not simultaneously 0.

Brief Description of the Drawings

[0014] The foregoing and other features and advantages of the invention will be apparent from the following, more particular description of various exemplary embodiments, as illustrated in the accompanying drawings wherein like reference numbers generally indicate identical, functionally similar, and/or structurally similar elements.

[0015] Figure 1 depicts the reversible redox-reaction of Benzoquinone-hydroquinone;

[0016] Figure 2 depicts the reversible redox behavior of a conductive porous nanostructured polyaniline film;

[0017] Figure 3 depicts the overlap between the electrochemical potential of conductive porous nanostructured polyaniline film and quinone;

[0018] Figures 4 and 5 compare the self-discharge behavior voltage of polyaniline-small molecule-quinone in supercapacitors with platinum current collectors showing;

[0019] Figure 6 depicts an image of nanostructured polyaniline-quinone;

[0020] Figure 7 shows a CV of nanostructured polyaniline-quinone showing the reversible redox behavior of the quinone-compound at 0.5 V vers Ag/AgCl;

[0021] Figure 8 shows the life cycle of nanostructured polyaniline-quinone compound;

[0022] Figure 9 compares CVs of poly-hydroquinone and polyhydroquinone with polyaniline on a metallic Pt-current collector. The addition of a small fraction of conducting polymer results in high electrochemical reversibility of the polyquinone and in some embodiments 10-30 times higher current (capacity) response;

[0023] Figure 10 shows an energy storage device according to an embodiment of the current invention;

[0024] Figure 11 shows an interpenetrating network used in a cathode according to an embodiment of the current invention;

[0025] Figures 12A and 12B compare the effects of using an interpenetrating network in a cathode material;

[0026] Figure 13 demonstrates that the specific energy density of a cathode material can be improved due to the high capacity of the polyquinone cathode according to an embodiment of the current invention;

[0027] Figure 14 shows a coin cell battery-lithium according to an embodiment of the current invention;

[0028] Figure 15 shows a CV of the coin cell battery from Figure 14;

[0029] Figure 16 describes the current process for manufacturing cathodes (and anodes) for Li-ion batteries;

[0030] Figure 17 shows a typical solvent casting system;

[0031] Figure 18 shows a schematic of the gravure process;

[0032] Figure 19 shows illustrations of some possible patterns for a gravure roll based process;

[0033] Figure 20 shows a schematic sketch of the circumferential grooves which can be used for the high speed roll in a gravure process;

[0034] Figure 21 shows a typical spray coating system;

[0035] Figure 22 shows energy densities/energy cost estimates for realistic fully packed battery cells according to an embodiment of the current invention; and

[0036] Figure 23 shows a comparison of energy cells.

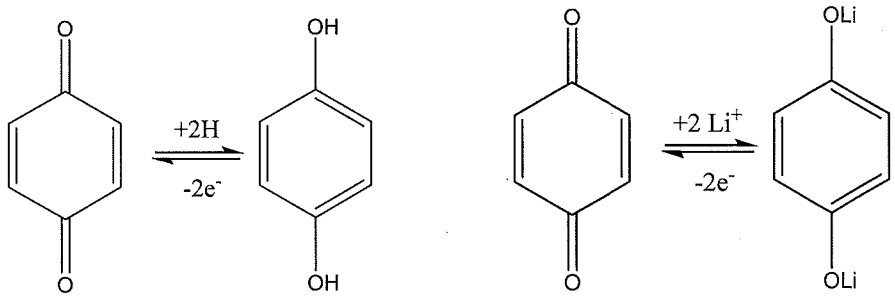
DETAILED DESCRIPTION

[0037] Some embodiments of the current invention are discussed in detail below. In describing embodiments, specific terminology is employed for the sake of clarity. However, the invention is not intended to be limited to the specific terminology so selected. A person skilled in the relevant art will recognize that other equivalent components can be employed and other methods developed without departing from the broad concepts of the current invention. All references cited anywhere in this specification, including the Background and Detailed Description sections, are incorporated by reference as if each had been individually incorporated.

Chemistry

[0038] Quinone redox compounds are highly reversible in water and organic solvents. The term quinone includes compounds having a fully conjugated cyclic dione structure, such as that of benzoquinones, derived from aromatic compounds by conversion of an even number of

number of –CH= groups into –C(=O)– groups with any necessary rearrangement of double bonds (polycyclic and heterocyclic analogues are included) (*e.g.*, 1,2-Benzoquinone, 1,4-Benzoquinone, 1,4-Naphthoquinone, and 9,10-Anthraquinone). The term quinone is also used more generally for a large class of compounds formally derived from aromatic quinones through replacement of some hydrogen atoms by other atoms or radicals (*e.g.*, Chloranil, Lawsone, and DDQ). This makes them suitable for use as cathodes in electrochemical cells with aqueous and organic electrolytic systems. Examples of Quinone redox reactions are shown in Scheme 1.



Water Based Reaction Reaction in Organic Solvents

Scheme 1

[0039] The theoretical electron charge-storage capacity of hydroquinone ("HQ") is 496 mAh/g, which is much higher than the capacity of nitroxyl radicals (111-147 mAh/g), polyaniline (244 mAh/g), PEDOT/PSS (< 41 mAh/g), or pyrenetetraquinone compounds (260-303 mAh/g). Of course, altering the structure of the quinone may add other beneficial properties, *e.g.*, HQ may have increased solubility and reversibility when sulfonated; however, the resultant charge-storage capacity is also decreased to 152 mAh/g. Accordingly, the selection and modification quinones and their derivatives is highly selective and complex.

[0040] The cyclic voltammogram ("CV") shown in Figure 1 describes the reversible redox-reaction of Benzoquinone-hydroquinone ("BQHQ"). The reversible redox-reaction results in high cycle-life for the electrochemical cell.

[0041] In order to facilitate charge transfer, HQ may be mixed with a conductive material, *e.g.*, polyaniline. The CV shown in Figure 2 describes the reversible redox behavior of a conductive porous nanostructured polyaniline film, which may be used as a conductive component to form an interpenetrating quinone cathode.

[0042] The CV shown in Figure 3 shows the overlap between the electrochemical potential of the conductive porous nanostructured polyaniline film and the quionone.

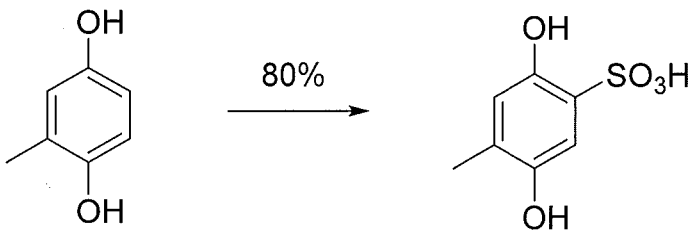
[0043] By creating a polyaniline-supercapacitor with quinones as electrolytes, the resultant supercapacitor was shown to remain stable over 50,000 galvonstatic charge-discharge cycles. This may occur because the quinones provide superior stability for the porous polyaniline material, *i.e.*, the porous polyaniline was not converted to a highly reactive state.

[0044] "Vonlanthen, D., Lazarev, P., See, K. A., Wudl, F. & Heeger, ***Adv. Mater.*** 26, 5095-5100, 2014" and **WO2015023974-A1**, each of which is incorporated by reference in its entirety, have shown that highly stable polymer-supercapacitors may be engineered by combining electrochemically active polymers and redox-active electrolytes with concerted electrochemical properties. In particular, the combination of HQBQ in an electrolyte solution increases the capacity of a polyaniline supercapacitor multiple times at both low and high discharge currents due to the high capacity of the quinone.

[0045] Moreover, the high mobility of small quinones allows the quinones to flow back and forth between the charged polyaniline electrode surface and cell, resulting in fast self-discharging of the electrochemical cell at an open potential (*e.g.* up to 6-20 times faster than in a polyaniline cell). This is shown more clearly in Figures 4 and 5 which compare the voltage of HQBQ polyaniline supercapacitors with platinum current collectors.

[0046] One method of incorporating HQ into a cathode is described below. The method involves incorporating free HQ, or its derivatives thereof, directly into the cathode material.

[0047] In this example, before incorporating the HQ into the cathode, the HQ was sulfonated as shown in Scheme 2. Scheme 2 shows an example of sulfonation, of 2-methyl-hydroquinone into 2,5-dihydroxy-4-methylbenzenesulfonic acid ("HQS") according to modified procedures from WO 03/027063 Al, US 3772379 A, EP 2313366 A2, each of which is incorporated by reference in its entirety.



Scheme 2

[0048] The resultant HQS was *in-situ* intercalated into conducting nano-fibers during electrochemical synthesis to give a nanostructured polyaniline-quinone, **material A**, Figure 6. **Material A** was formed with 1 equivalent of quinone per polyaniline repeat unit, which was confirmed by elemental analysis.

[0049] Figure 7 shows a CV of **material A**, where an additional redox peak, from the HQS, occurred between the two redox peaks of polyaniline.

[0050] The cycling stability of the quinone/conductive polymer composite was very high due to the intercalated HQS, for more than 10,000 cycles, as shown in Figure 8. However, the capacity was lower than the pure polyaniline due to the low capacity of small molecule compound which bears a sulfonic acid group at each quinone-unit.

[0051] Conductive polymer include polymers that are intrinsically electrically conducting (including metallic or semiconducting units).

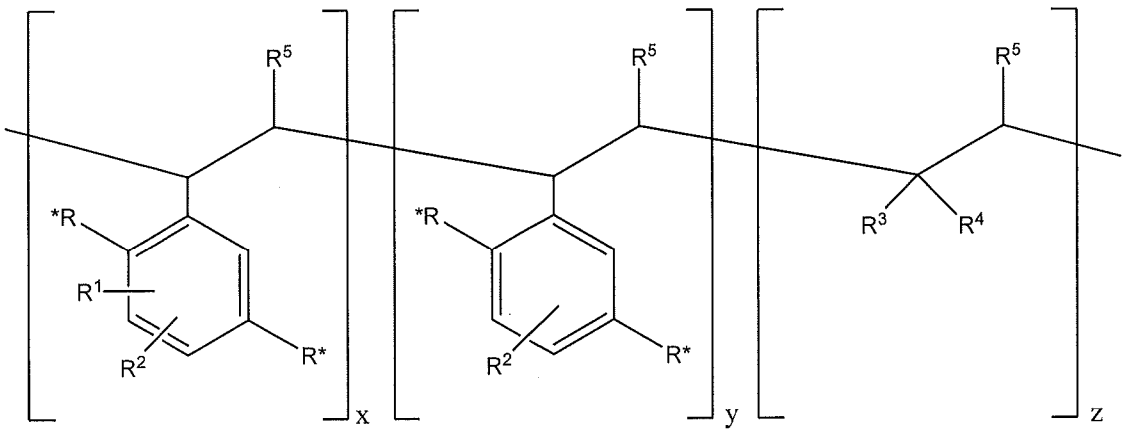
Polymers

[0052] Another solution for incorporating BQHQ into a supercapitor, is to incorporate BQHQ as a polymer, *e.g.*, poly(hydroquinone) ("pHQ"), which has a charge-storage capacity of 392 mAh/g. pHQ may be beneficial because it is soluble in alcohols; and water or other desirable solvents when at least partially sulfonated. Partially sulfonated pHQ ("pHQS") has a capacity of 329 mAh/g, which is still much higher than traditional metal cathodes. Moreover, the partial sulfonation enhances the ionic conductivity of the cathode, which may thereby improve the power-out of the electrochemical cell and the stability of the Quinone-conducting polymer-network.

[0053] pHQ may be considered a type of redox-active polymer, *i.e.*, a polymer which possess redox properties (reversible or not), although pHQ does possess reversibility. The term capacitive polymer may be used interchangeably with reversible redox-active polymer, and may further include polymer which have the ability to store electric charge.

[0054] The term polymer is meant to include any large molecule composed of many repeated units. In some embodiments the polymers may have more than 50 or 100 units, in other embodiments polymers may have more than 1000 units, or even more than 10,000 units. Some embodiments provide polymers having between 100-1,000,000 units, 1,000-1,000,000 units, 10,000-1,000,000 units, or even 100-1,000 units. In embodiments polymers may be defined by their molecular weight, accordingly, polymers may have a weight greater than 3,000 Daltons, in other embodiments polymers may have a weight greater than 10,000 Daltons, or even 100,000 or 1,000,000 Daltons. Certain embodiments provide polymers having a molecular weight of between 5,000-1,000,000 Daltons or 3,000-100,000 Daltons.

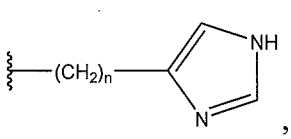
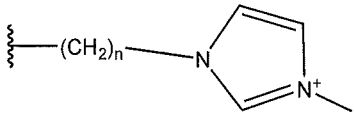
[0055] Accordingly, one aspect of the present application provides polymers having formula (I):



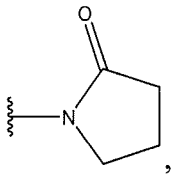
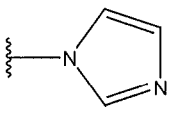
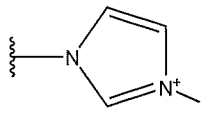
(I)

wherein:

each R*, independently, is OR^a, =O , O-alkyl, $-OCO_2R^4$, -O-silyl group, or a protected hydroxyl group;

each R^1, independently, is $-SO_3R^a$, $-CO_2R^a$, haloalkyl, $-(CH_2)_n-N(R^6)_2$, $-(CH_2)_n-PO_3R^a$,  ,  , $-SO_2N(R^5)_2$, $-SO_2R^5$, $-N(SO_2R^6)_2$, $-N(SO_2CF_3)_2$, -CN, halo, or nitro;

each R^2, independently, is H, alkoxy, alkyl, halo, cyano, haloalkyl, or nitro;

each R^3, independently, is alkyl, aryl, $-(CH)_2CO_2R^5$, -OH, $-OC(=O)R^6$, $-C(=O)NHR^5$, $-NHC(=O)CH_3$, $-(CH_2)_mSO_3R^a$, $-(CH_2)_m-PO_3R^a$, $-(CH_2)_mN^+(R^4)_3$,  ,  ,  , $-C(=O)NH-C(CH_3)_2-CH_2SO_3R^a$, $-C(=O)NH(CH_2)_3N^+(CH_3)_2-(CH_2)_3SO_3^-$, or -CN;

each R^4, independently, is H, alkyl, halo, or haloalkyl;

each R^5, independently, is H or alkyl;

each R^6, independently, is alkyl or aryl;

each R^7, independently, is alkyl;

each R^a is e^-, H, or a cation;

n is 0, 1, 2, 3, or 4; m is 0, 1, 2, or 3; x is greater than 0 and no greater than 1; y is no greater than 1; and z is 0 to 0.5. x + y + z = 1, provided that x and z are not simultaneously 0.

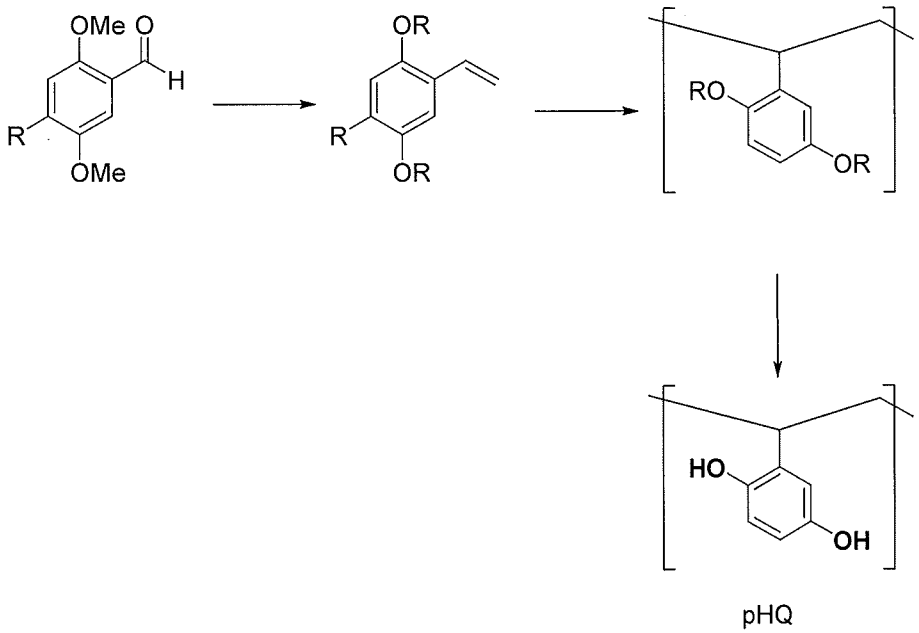
[0056] In some embodiments, x is no greater than 0.5 and z is no greater than 0.1, or, in some embodiments, x can be no greater than 0.2 and z can be no greater than 0.1. In some embodiments, z can be 0.

[0057] In some embodiments, each R^1 can be $-SO_3R^a$ and each R^2 can be H.

[0058] In some embodiments, x can be 1, each R^1 can be $-SO_3R^a$, and each R^2 can be H.

[0059] A polymer of formula (I) (e.g., where R^1 is $-SO_3H$) can be made by including a suitable co-monomer when forming pHQ, followed by sulfonation of the co-polymer.

[0060] In order to create polymers of formula (I), pHQ was first synthesized in high yield without the use of any expensive reagents or purification steps according to EP 0 532 192 A1 (which is incorporated by reference in its entirety) starting from a commercially available inexpensive chemical, described in Scheme 3 below.

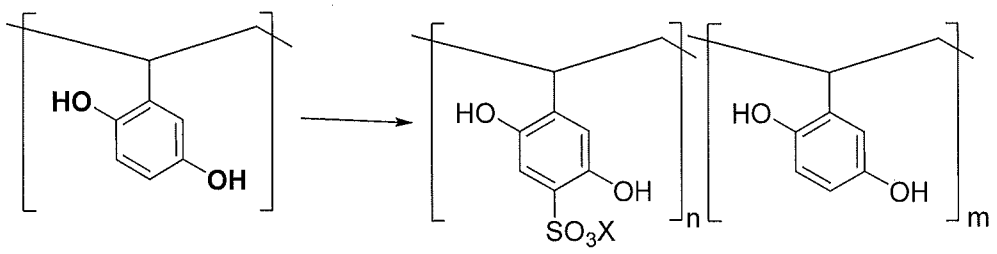


pHQ

Scheme 3

[0061] The partial sulfonation of the quinone-polymer was achieved with chloro-sulfonic acid, where the degree of sulfonation is determined by the ratio of sulfonation reagent and poly-quinone. The solubility and ionic conductivity is then determined by the degree of sulfonic acid groups in pHQS (structure 101), as shown in Scheme 4. In structure 101,

n+m=1 and n can be from about 0 to about 0.5, in some embodiments about 0.05 to about 0.2.



pHQ pHQS (101)

Scheme 4

[0062] As shown in Figure 9, a pure pHQ film shows irreversible redox behavior and low current giving a low capacity and low cycling stability. However, as also shown in Figure 9, when pHQ is dispersed in a conducting polymer matrix, *e.g.*, polyaniline, the material demonstrates highly reversible redox behavior. The higher current shows the increased capacity of the quinone polymer due to the interpenetrating polymer network system. The CVs in Figure 9 were performed, with a Pt counter electrode vs Ag/AgCl.

[0063] The term interpenetrating network is intended to include networks of two or more types of polymers which are at least partially interlaced on a molecular level. In some embodiments, these networks may be analogous to fibers in a cloth, where each fiber is a polymer; in such embodiments, the distribution of fibers may be random, partially random, or patterned. In some embodiments, the network provides multiple pathways between two locations within the network. If there is a break anywhere along one pathway between the two locations, there will often be one or more remaining pathways between the two locations. A communications network, *e.g.* , the internet, is another example of an analogous network. If one server or communication link goes down, there remain alternative pathways for the message to travel from the sender to the receiver. An electrode that has an interpenetrating network of conducting polymer chains can provide the network with integrity for conducting electricity through it since the network can not only have flexibility resisting breaking of the polymer chains, but even some breakage can be tolerated due to the fact that additional conducting paths will usually be available. In the case of an interpenetrating network with

conducting polymers and capacitive polymers, charge transfer between the two types of polymers can occur throughout the bulk of the network in such a way as to maintain integrity as mentioned above. In some embodiments, the interpenetrating networks can function so as to prevent one polymer from dissolving, or leaving the bulk of the interpenetrating network. Some interpenetrating networks may have the property that the two or more polymers resist being pulled apart and/or that electrons may be transferred between interlaced polymers. In some embodiments, one polymer may be completely or mostly interlaced within the body of a second polymer and/or the interpenetrating networks may be a homogenous network. In some embodiments, interpenetrating networks are formed between reversible redox active polymers and conductive polymers, in some embodiments, there may be multiple points of interaction between the redox polymer and the conductive polymer. In additional embodiments, a plurality of conductive polymers may interact with multiple sites of a single redox polymer and vice versa, or a combination thereof.

[0064] In some embodiments the ratio of capacitive polymer to conductive polymer is between 99.5:0.5 to 95:5 or in other embodiments 97:3 to 50:50, in other embodiments between 90:10 and 85:15, or even between 85:15 and 65:35. Still other embodiments provide for ratio between 65:35 and 50:60 or even between 50:60 and 10:80.

[0065] In certain embodiments higher densities are preferable to give higher volumetric densities. Additionally, in some embodiments higher porosities of the conducting polymer may be beneficial of achieve higher ion transport.

Composite Material

[0066] Another embodiment, the present invention provides a composition that includes an interpenetrating network of the polymer of formula (I) and a conducting polymer. The composition may further include a solvent.

Conducting Polymers

[0067] The conducting polymer can be PEDOT, a polyaniline, a polythiophene, or a combination thereof.

Solvents

[0068] The solvent can be water and optionally include a co-solvent. In some embodiments, the co-solvent can be, for example, a lower alcohol, NMP, DMSO, or DMF.

Energy Storage Device

[0069] Another embodiment of the present invention provides an energy storage device comprising a cathode having a polymer of formula (I); an electrolyte; and an anode. Figure 10 shows an example of such an energy storage device, where the electrolyte 104 is in-between cathode 103 and anode 104.

Cathode

[0070] In some embodiments, the cathode materials can include a conducting polymer. Moreover, the cathode material can further include one or more of: (i) a metal oxide nano powder; (ii) a carbon material selected from graphene oxide, graphitized carbon, graphite particles, carbon nanotubes, and carbon nanoparticles, or a combination thereof; and (iii) a binder selected from PVDF, CMC, PTFE, PEO and poly(vinyl alcohol), or a combination thereof.

[0071] In some embodiments, the polymer of formula (I) and the conducting polymer are crosslinked. The crosslinker can be glutaraldehyde, (3-glycidyloxypropyl)trimethoxysilane, dithiobis(succinimidyl propionate), disuccinimidyl suberate, or any other bifunctional cross-linking unit.

[0072] Generally, the capacitive polymer forms a hierarchical interpenetrating network with the conductive polymer, as can be seen in Figure 11. In Figure 11, cathode 103 is formed from a conducting polymer 107, quinone polymer 101, and cross-linkers 108. The nanostructures formed in such a cathode may conduct electrons through the three-dimensional bulk space of the electrode.

[0073] As can be seen in Figure 12A, when the capacitive polymers in the cathode are interpenetrated and optionally cross-linked, they stay within the cathode which gives a high battery cycling stability. In contrast, Figure 12B shows what happens when there is no interpenetrating network, and the cathode "dissolves" into the electrolyte and the battery degrades. This normally happens with most small molecule and polymer-quinones using conventional carbon conductors, and also with sulfur and other small capacitive particles. That is, the interpenetrating polymers, may prevent the quinone polymer 101 from dissolving into the electrolyte body of an energy storage device.

[0074] In some embodiments with cross-linkers, the amount of cross-linking necessary may be minimal. By reducing the amount of cross-linking, the quinone polymer 101 may maintain a higher capacity for its electron-exchange reactions. Notably, low fraction cross-linking is difficult to achieve with inert conventional carbon conductors.

[0075] In some embodiments, the cathode material may form a gel structure with or without cross-linking if more solvent molecules are absorbed. Benefits of such embodiments may improve ion conduction in the cathode, which may further improve power-output.

[0076] In some embodiments, a mediator-effect may be provided by the conductive surface. In certain embodiments, this allows the redox process for the quinone units in the cathode to exhibit greater reversibility, which may enhance the cycling stability of the electrochemical device, more information on this effect may be seen in PCT/US2014/051330, which demonstrated functionality over 50,000 cycles.

[0077] Interestingly, sulfonic acid groups in the quinone polymer may help prevent inter-tangling of the redox-polymer, which allows more access to the theoretical capacity of the polymer.

[0078] In some embodiments, the cathode may be less susceptible to cracks, as compared to traditional inorganic cathodes, for the reason that the active and conductive materials are soft.

[0079] In some embodiments, the cathode may include one or more additives to improve device performance and/or process-ability. Examples of additives can include:

[0080] First, metal oxide nano powders such as Al_2O_3, TiO_2, and SiO_2 (Nanoparticles, nanotubes, nanorods) as dispersions which can be used as additives to improve the A) performance of the redox-process; B) adhesion of the polymer composite; and C) enhance the ionic conductivity and improve the viscosity giving improved process-ability of the solution. The metal oxide/polymer composite may be used in a weight ratio of between 0:100 and 30:80 and in some embodiments between 0:100 and 10:90.

[0081] Second, carbon based materials including graphene oxide, graphitized carbon, graphite particles, carbon nanotubes and nanoparticles, which can be well dispersed within the quinone polymer and the conducting polymer in water or polar solvents. These additives may further improve the process ability and performance of the cathode due to enhanced surface, electric conductivity and enhanced formation of a gel/viscous solution suitable for solution processing forming homogenous cathodes films. The additive/polymer composite can be used in any weight ratio. In some embodiments a weight ratio of between 0:100 and 30:80 and in other embodiments between 0:100 and 5:95.

[0082] Third, while the conducting polymer may act as a binder by itself, additional binders may improve the mechanical stability of the composite and improve the solution processability. Examples of binders can include PVDF, CMC, PTFE, PEO or polyvinylalcohol.

[0083] Fourth, cross-linkers may be added. In particular, a small degree of cross-linking between the quinone-polymer and conducting polymer can improve stability of the cathode. Additionally, low fraction cross-linking increases the mechanical stability of the cathode (solubility changes during charge and discharge processes). Only a few positions in the network need to be cross-linked due to the relatively high chain length of the polymers. The low fraction cross-linking has the advantage that the majority of the reactive sites of the polymers are not chemically deactivated and the capacitive polymer chains can still rearrange (low rigidity) themselves to maintain a high capacity. The cross-linking can be carried out, for example, during the casting process. Furthermore, the low fraction cross-linking can improve the wet adhesion to the metal current collector.

[0084] Examples of suitable crosslinkers include glutaraldehyde, (3-glycidyloxypropyl)trimethoxysilane, dithiobis(succinimidyl propionate), disuccinimidyl suberate or other bifunctional cross-linking units with a molecular weight between 80 and 550 g/mol. The cross-linker/polymer composite can be used in a weight ratio of between 0:100 and 10:90 and in some embodiments in a range of 0:100 to 3:97.

Anode

[0085] The anode may be any material that has a greater electropositive potential than cathode.

Electrolyte

[0086] The electrolyte can be any liquid or solid that transports ionic charges between the both electrodes.

Comparison

[0087] A comparison of conventional active cathode materials, shown in Figure 13, demonstrates that the specific energy density can be improved due to the high capacity of the polyquinone cathode (the energy densities are calculated considering only the active cathode materials vs Li/Li^+).

[0088] Moreover, the provided cells may be safer than other cells with comparable energy density (*i.e.*, they use high voltage to achieve the same energy density) as the operation voltage is around 2.7-3 V but not higher. The low voltage cells results in less decomposition of the electrolytes. This results in a higher cycle-life.

Coin Cell Battery

[0089] Composite materials, as previously described, were incorporated into coin cell batteries as shown in Figure 14. A CV of the resultant lithium cell is shown in Figure 15. The polymer composite specifically used was pHQ/PEDOT:PSS/Ketjenblack® in a ratio of 2:2:1 and measured with lithium as the anode. The CV demonstrated the reversible quinone redox

behavior at a high potential of 3.03V v. Li/Li^+ which is comparable to the redox-potential of small molecule-quinone in the literature.[3]

Manufacture of Energy Storage Devices

[0090] Figure 16 describes the current process for manufacturing cathodes (and anodes) for Li-ion batteries. The first stage is to mix the electrode materials with a conductive binder to form a slurry which is spread on the surface of the foil as it passes into the machine. A knife edge is located just above the foil and the thickness of the electrode coating is controlled by adjusting the gap between the knife edge and the foil. Since it is not unusual for the gravimetric or volumetric energy storage capacity of the anode material to be different from that of the cathode material, the thickness of the coating layers must be set to allow the energy storage per unit area of the anode and cathode electrodes to be matched.

[0091] This is an inefficient, complex and expensive process due to the fact that the material to be adhered to the substrate is a nonhomogeneous suspension or a slurry. When the solvent is removed from the slurry, the resulting film is rough, instead of being coalesced, as needed. This issue is currently being addressed by calendaring (compressing), but the surface cannot be made as good as with true solution casting, and micro voids may be created between the particles. Furthermore, commercial calendars tend to be expensive and difficult to maintain, and winding needs to occur before complete drying to avoid cracking of the electrodes.

[0092] Fortunately a polymer of formula (I) can be used as the cathode material to produce highly performing energy storage devices. The unique properties of this cathode material allow use of manufacturing processes that are less expensive than those of existing processes employed in Li-ion battery manufacturing. None of the conventional cathode materials can be processed using the methods described herein.

[0093] The polymer of formula (I) has a very significant advantage in that it can be formulated as a homogeneous suspension in several industry standard solvents, including inexpensive, non-toxic solvents (e.g., water, lower alcohols, mixtures of these, and the like).

This leads to manufacturing processes which are more efficient, more cost effective, and produce a higher quality product.

[0094] In another embodiment, a method of making an energy storage device includes depositing the polymer of formula (I) on a current collector. The current collector can be a metal foil substrate, wherein the metal is selected from copper, titanium, or aluminum foil.

[0095] In some embodiments, depositing includes depositing a solution of the polymer. Depositing the solution can include gravure roll coating; or can include spray coating.

[0096] In another embodiment, a method of making a cathode film includes depositing the polymer of formula (I) on a release film. The release film can be a non-stick film. The non-stick film can include a TFE polymer, a CTFE polymer, an ETFE polymer, or an ECTFE polymer; for example, a Teflon FEP film or Teflon PFA film.

[0097] Generally, high capacity redox-polymers form interpenetrating networks with conducting polymers to give superior solution-processable cathodes, which may be used in, for example, supercapacitors and batteries. The low-cost cathode has improved properties due to solubilizing groups. The novel design of the organic cathode can provide high energy electrochemical cells with improved power density and lowered capacity fade and low self-discharge. Moreover, the design of the organic cathode has high electric conductivity and makes good contact to the current collector which results in lowered loss of electric charge during charge and discharge of the electrochemical cell. The cathode is manufactured by solvent casting, printing or spraying.

Solvent Casting

[0098] Figure 17 shows a typical solvent casting system. The process is less expensive than the process currently used to manufacture electrodes of conventional Li-ion batteries, however the process cannot be used to produce Li-ion cathodes of the existing technology because the cathodes are made from a slurry or nonhomogeneous suspension.

[0099] Although solvent casting is known in the art, it has not been used to continuously form cathode films (on a substrate or free standing). Cathode films based on polymers of

formula (I) can be manufactured using a modified solvent casting process where the solvent evaporation is allowed to occur at the heating temperature well below the point at which the nanostructure of the polymer of formula (I) electrode is damaged.

[00100] When dissolved, the polymer of formula (I) material produces a homogeneous mixture. Once the solvent is evaporated by the continuous solvent casting process, the resulting product is a homogeneous film having a controlled thickness and width. During the evaporation process, the solids coalesce to develop an extremely smooth surface. This process is relatively simple, inexpensive, and environmentally clean with water as a possible solvent. The resulting film can be immediately laminated to another film at the exit of the solvent casting machine. Winding of the resulting film can be done at any time without risk of cracking.

Gravure Roll Coating

[00101] Another simple manufacturing method utilizing unique properties of the presently described cathode material is similar to that of the rotary gravure printing process that can be successfully adopted to manufacture cathode films or coatings using the polymer of formula (I).

[00102] A schematic of the gravure process is shown in Figure 18. The gravure cylinder picks up the electrode material solution in precisely constructed tiny indentations covering the entire surface of the roll. And the excess is wiped off by the doctor blade. Gravure based processing up to this time has only been used for printing, where these indentations are only on the area to be printed. For use in cathode production, the depth of the indentations control the thickness of the coating.

[00103] The input would be the substrate (conductor) film instead of paper. The impression roll is used as a means for exerting uniform pressure on to the substrate film so it picks up the 'printing' evenly. The doctor blade wipes off any excess solution/suspension. The ink fountain is filled with the solution/suspension liquid material.

[00104] The surface or the gravure roll should be a very fine grid, perhaps several hundred lines per inch. Within each compartment, there should be an indentation to carry the

solution/suspension. This process does produce a very uniform coating on to the substrate. An illustration of some possible patterns are shown in Figure 19.

[00105] The number, type, and depth of these indentation must be optimized to provide the desired thickness of the coating and to assure the best coalescence.

[00106] A gravure roll produced to the proper specifications can be made by a chemical etch process as currently used to produce gravure rolls.

[00107] Once coated, the substrate/coating film may be dried by one of several means:

1. Passing the film over a heated roll (coating side up)
2. Passing the film on a belt using radiant heat
3. Passing the film on a belt using air dry heated or ambient using free of forced convection

[00108] Figure 20 shows a schematic sketch of the circumferential grooves which can be used for the high speed roll of a machine direction film orientation machine. At a surface speed of about 300 feet per second an air layer would be introduced between the film and the roll causing the roll to lose its grip on the film. This would drastically reduce the heat transfer rate and allow a high degree of neck-in which would result in a cross section of the film looking like that of a concave lens.

[00109] The cross section across the film should be of a constant thickness; in other words, a film of uniform gauge is desired. This will keep the properties uniform across the film and assure winding a high quality roll with no wrinkles or possibility of telescoping.

[00110] The grooves shown in Figure 20 have a size in the range of several hundred grooves per linear inch. The flat top surface maintains the roll/film grip as well as good heat transfer and the space between each groove allows the air to pass through and there are no visible markings on the film. Figure 20 is taken from US patent 4,428,724, which is incorporated by reference in its entirety.

Spray Coating

[00111] Another method of depositing the polymer of formula (I), is the use of coating on a conveyer by continuous flat fan spraying. Figure 21 shows a typical spray coating system where spray bar of multiple flat fan nozzles are shown. The spray patterns slightly overlap to compensate for spraying thus giving a uniform bar of spray. The conveyor moves product under full cure spray for set period of time before moving on. This process cannot be used for slurries of suspensions because these materials would clog the nozzles. This has an advantage of continuous or intermittent coating.

Example

[00112] High level calculation were performed to estimate energy densities and energy costs of realistic fully packed battery cells as shown in Figure 22. The model was adopted from Park, M. S.; Ma, S. B.; Lee, D. J.; Im, D.; Doo, S.-G.; Yamamoto, O. *Sci. Rep.* **2014**, *4*. (basic physical parameters). Additional parameters and assumptions were made to obtain energy densities and energy costs for a mass produced bare secondary lithium cell. The following were considered.

a) The real potential of lithium-intercalation at the anode of choice was considered.

b) Current collectors were 12 μm for aluminum (Cathode) and 8 μm for copper (Anode).

c) Electrolyte: $LiPF_6$ 1.2M in EC/EMC

d) Polymer Separator: 1 mg/cm^2

e) In the case of cells with a LTO anode both current collectors were aluminum (12 μm).

f) For the capacity of the polymer cathode the maximum possible value was assumed.

g) The voltage of the polyquinone-lithium redox reaction at the cathode was taken from the Literature.[3] The potential of the quinone-lithium reactions at the cathode 103 was 2.7 V vs Li/Li^+.

h) The film thickness was kept constant (75 μm) for all cathodes. For the high power-cells (Vonlanthen-Heeger Cell 2 and 3) the electrode thickness was reduced by 75%.

i) The packaging was therefore calculated as an additional entity. The bare cell pack was calculated to be approximately 5% of the total cell weight.

j) Capacities and potentials of the intercalation reaction of the inorganic cathodes were taken from the scientific literature at a discharge rate of 1C.

k) Labor and overhead costs (12%) were added to the total cost. This includes the entire mass production process of the battery cells, including personal cost, all purchased materials and inefficiencies like wasted materials during the production process (all variables costs)

l) The production plant was considered to be available. Therefore capital costs of the production plant were not included in the cost calculation.

m)It was assumed that the batteries can be made in mass production using existing production plants.

n) Cost of materials was available from Argonne National Laboratory.

[00113] The results for 3 types of cells are provided below, and a comparison of each along with conventional cells is provided in Figure 23.

Vonlanthen-Heeger Cell 1 (High Energy Density configuration)
Polymer-Cathode and Graphite-Anode
Gravimetric Energy Density: 459 Wh/kg
Energy costs: $54/kWh

Vonlanthen-Heeger Cell 2 (High energy and power density configuration)
Polymer-Cathode and Graphite-Anode
Gravimetric Energy Density: 358 Wh/kg
Energy Cost: $85/kWh

Vonlanthen Heeger Cell 3 (High power configuration)
Polymer-Cathode and LTO-Anode
Gravimetric Energy Density: 115 Wh/kg
Energy Cost: $171/kWh

[00114] Other metal anodes are also suitable, such as Li metal, Mg, Na, Zn, any carbon other than graphite, Si, Sn and their intercalation anodes which are more electropositive than the active cathode material.

References

[00115] Each of the following references is incorporated by reference in its entirety.

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Claims

1. An energy storage device, comprising:

a cathode;

an anode spaced apart from said cathode; and

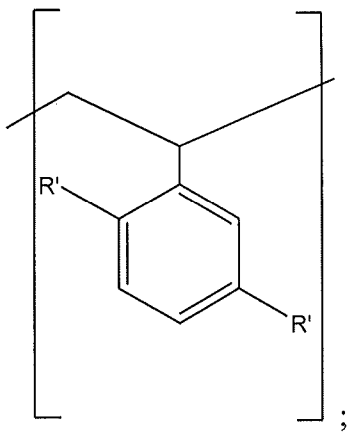
an electrolyte in contact with said anode and said cathode;

wherein said cathode comprises a capacitive polymer and a conductive polymer;

wherein said capacitive polymer comprises an alkane chain backbone with pendant quinone units; and

wherein said capacitive polymer and said conductive polymer form an interpenetrating network.

2. The energy storage device of claim 1, wherein said capacitive polymer is polyvinyl hydroquine having a structure of:



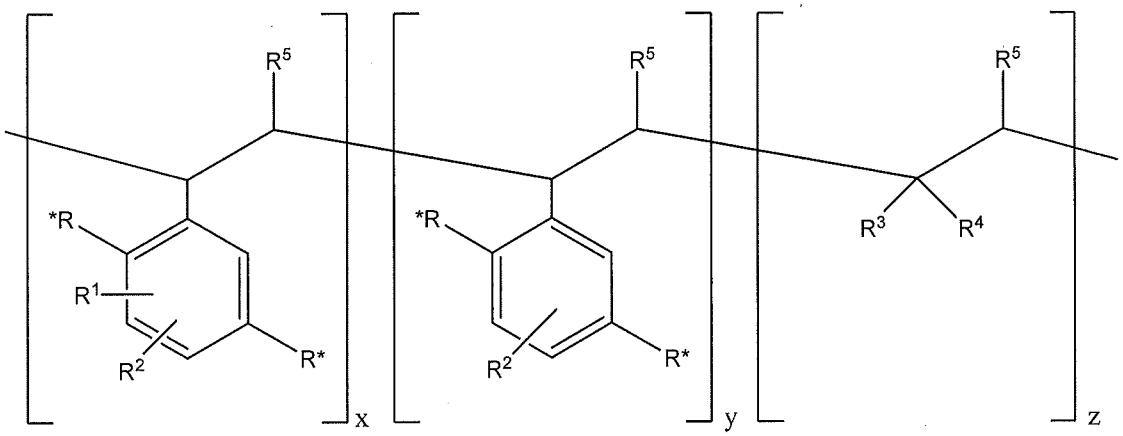
;

wherein:

each R', independently, is selected from the group consisting of OR^a or =O; and

each R^a is e^-, H, or a cation.

3. The energy storage device of claim 1, wherein said capacitive polymer has a structure of Formula (I)

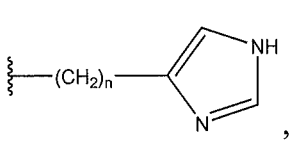


Formula (I)

wherein:

each R*, independently, is OR^a, =O , O-alkyl, $-OCO_2R^4$, -O-silyl group, or a protected hydroxyl group;

each R^1, independently, is $-SO_3R^a$, $-CO_2R^a$, haloalkyl, $-(CH_2)_n-N(R^6)_2$, $-(CH_2)_n-PO_3R^a$,



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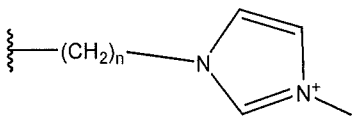
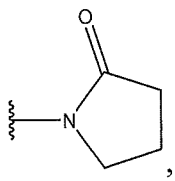


R^7, $-SO_2N(R^5)_2$, $-SO_2R^5$, $-N(SO_2R^6)_2$, $-N(SO_2CF_3)_2$, -CN, halo, or nitro;

each R^2, independently, is H, alkoxy, alkyl, halo, cyano, haloalkyl, or nitro;

each R^3, independently, is alkyl, aryl, $-(CH)_2CO_2R^5$, -OH, $-OC(=O)R^6$, $-C(=O)NHR^5$,

$-NHC(=O)CH_3$, $-(CH_2)_mSO_3R^a$, $-(CH_2)_m-PO_3R^a$, $-(CH_2)_mN^+(R^4)_3$,



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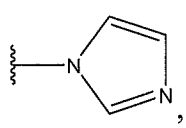
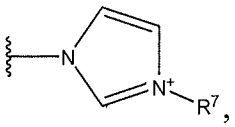
 ,  , -C(=O)NH-C(CH_3)$_2$-$CH_2SO_3R^a$, C(=O)NH$(CH_2)_3N^+(CH_3)_2$-$(CH_2)_3SO_3^-$, or -CN;

each R^4, independently, is H, alkyl, halo, or haloalkyl;

each R^5, independently, is H or alkyl;

each R^6, independently, is alkyl or aryl;

each R^7, independently, is alkyl;

each R^a is e^-, H, or a cation;

n is 0, 1, 2, 3, or 4;

m is 0, 1, 2, or 3;

x is greater than 0 and no greater than 1;

y is no greater than 1; and

z is from 0 to 0.5;

wherein x + y + z = 1, provided that x and z are not simultaneously 0.

4. The energy storage device of anyone of claims 1-3, wherein said conducting polymer is PEDOT, a polyaniline, a polythiophene, or a combination thereof.

5. The energy storage device of anyone of claims 1-4, wherein the cathode further comprises at least one of:

a metal oxide nano powder;

a carbon material selected from graphene oxide, graphitized carbon, graphite particles, carbon nanotubes, and carbon nanoparticles, or a combination thereof; and

a binder selected from PVDF, CMC, PTFE, PEO and poly(vinyl alcohol), or a combination thereof.

6. The energy storage device of claim 4, wherein said capacitive polymer and said conductive polymer are crosslinked.

7. The energy storage device of claim 6, wherein the crosslinker comprises glutaraldehyde, (3-glycidyloxypropyl)trimethoxysilane, dithiobis(succinimidyl propionate), disuccinimidyl suberate, or any other bifunctional cross-linking unit.

8. An electrode, for use as a cathode, comprising:

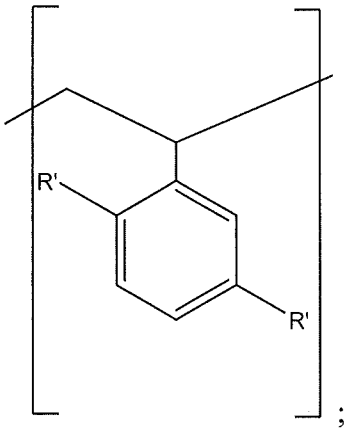
a capacitive polymer; and

a conductive polymer;

wherein said capacitive polymer comprises an alkane chain backbone with pendant quinone units; and

wherein said capacitive polymer and said conductive polymer form an interpenetrating network.

9. The electrode of claim 8, wherein said capacitive polymer is polyvinyl hydroquine having a structure of:



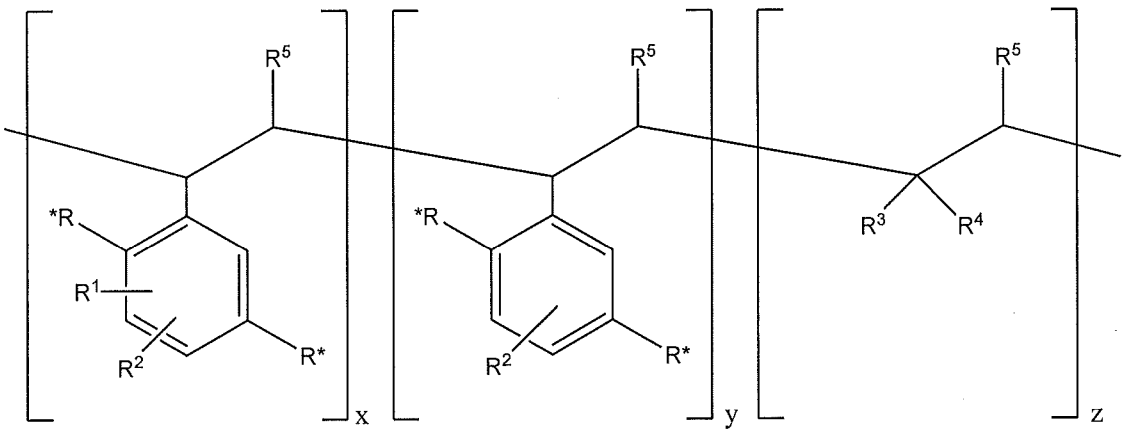
;

wherein:

each R', independently, is selected from the group consisting of OR^a or =O; and

each R^a is e^-, H, or a cation.

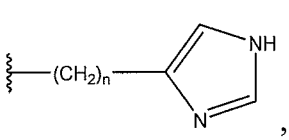
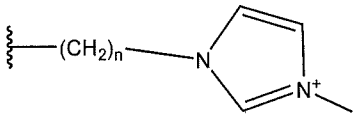
10. The electrode of claim 8, wherein said capacitive polymer has a structure of Formula (I)



Formula (I)

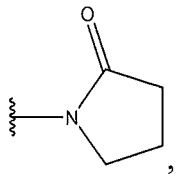
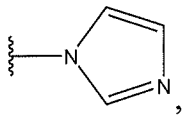
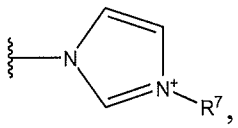
wherein:

each R*, independently, is OR^a, =O , O-alkyl, $-OCO_2R^4$, -O-silyl group, or a protected hydroxyl group;

each R^1, independently, is $-SO_3R^a$, $-CO_2R^a$, haloalkyl, $-(CH_2)_n-N(R^6)_2$, $-(CH_2)_n-PO_3R^a$,  ,  , $-SO_2N(R^5)_2$, $-SO_2R^5$, $-N(SO_2R^6)_2$, $-N(SO_2CF_3)_2$, -CN, halo, or nitro;

each R^2, independently, is H, alkoxy, alkyl, halo, cyano, haloalkyl, or nitro;

each R^3, independently, is alkyl, aryl, $-(CH)_2CO_2R^5$, -OH, $-OC(=O)R^6$, $-C(=O)NHR^5$,

 , $-NHC(=O)CH_3$, $-(CH_2)_mSO_3R^a$, $-(CH_2)_m-PO_3R^a$, $-(CH_2)_mN^+(R^4)_3$,  ,  , $-C(=O)NH-C(CH_3)_2-CH_2SO_3R^a$, $C(=O)NH(CH_2)_3N^+(CH_3)_2-(CH_2)_3SO_3^-$, or -CN;

each R^4, independently, is H, alkyl, halo, or haloalkyl;

each R^5, independently, is H or alkyl;

each R^6, independently, is alkyl or aryl;

each R^7, independently, is alkyl;

each R^a is e^-, H, or a cation;

n is 0, 1, 2, 3, or 4;

m is 0, 1, 2, or 3;

x is greater than 0 and no greater than 1;

y is no greater than 1; and

z is from 0 to 0.5;

wherein x + y + z = 1, provided that x and z are not simultaneously 0.

11. The electrode of anyone of claims 8-10, wherein said conducting polymer is PEDOT, a polyaniline, a polythiophene, or a combination thereof.

12. The electrode of anyone of claims 8-11, further comprises at least one of:

a metal oxide nano powder;

a carbon material selected from graphene oxide, graphitized carbon, graphite particles, carbon nanotubes, and carbon nanoparticles, or a combination thereof; and

a binder selected from PVDF, CMC, PTFE, PEO and poly(vinyl alcohol), or a combination thereof.

13. The electrode of claim 11, wherein said capacitive polymer and said conductive polymer are crosslinked.

14. The electrode of claim 13, wherein the crosslinker comprises glutaraldehyde, (3-glycidyloxypropyl)trimethoxysilane, dithiobis(succinimidyl propionate), disuccinimidyl suberate, or any other bifunctional cross-linking unit.

15. A method of producing an energy storage device, comprising:

providing a composition containing a capacitive polymer and a conductive polymer;

depositing said composition on a current collector;

placing an anode spaced apart from said composition;

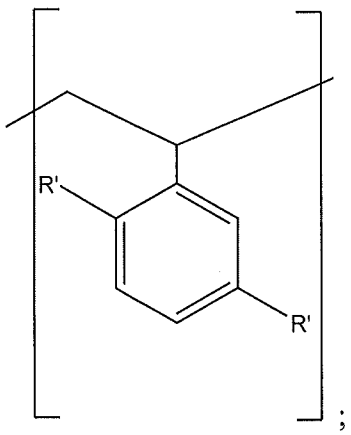
providing an electrolyte in contact with said composition and said anode;

wherein said capacitive polymer comprises an alkane chain backbone with pendant quinone unit; and

wherein said capacitive polymer and said conductive polymer form an interpenetrating network.

16. The method of claim 15, further comprising crosslinking said capacitive polymer and said conductive polymer.

17. The method of claim 15, wherein said capacitive polymer is polyvinyl hydroquine having a structure of:



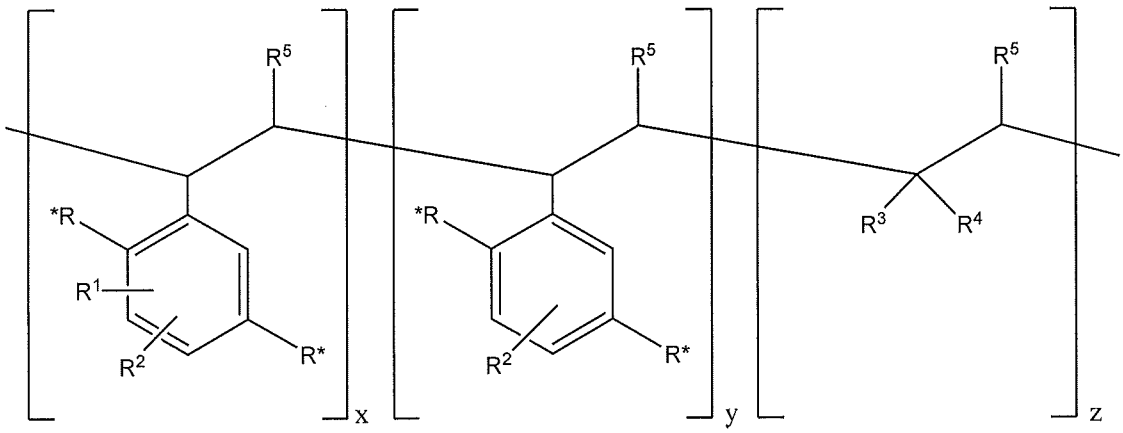
;

wherein:

each R', independently, is selected from the group consisting of OR^a or =O; and

each R^a is e^-, H, or a cation.

18. The method of claim 15, wherein said capacitive polymer has a structure of Formula (I)

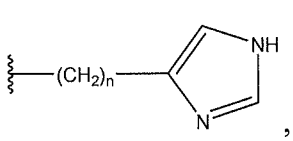


Formula (I)

wherein:

each R*, independently, is OR^a, =O , O-alkyl, $-OCO_2R^4$, -O-silyl group, or a protected hydroxyl group;

each R^1, independently, is $-SO_3R^a$, $-CO_2R^a$, haloalkyl, $-(CH_2)_n-N(R^6)_2$, $-(CH_2)_n-PO_3R^a$,



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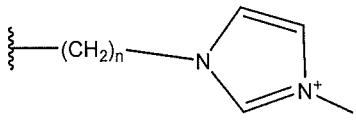
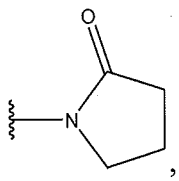


, $-SO_2N(R^5)_2$, $-SO_2R^5$, $-N(SO_2R^6)_2$, $-N(SO_2CF_3)_2$, -CN, halo, or nitro;

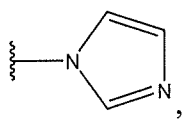
each R^2, independently, is H, alkoxy, alkyl, halo, cyano, haloalkyl, or nitro;

each R^3, independently, is alkyl, aryl, $-(CH)_2CO_2R^5$, -OH, $-OC(=O)R^6$, $-C(=O)NHR^5$,



,

$-NHC(=O)CH_3$, $-(CH_2)_mSO_3R^a$, $-(CH_2)_m-PO_3R^a$, $-(CH_2)_mN^+(R^4)_3$,



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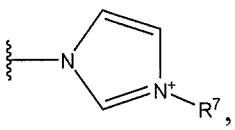


, $-C(=O)NH-C(CH_3)_2-CH_2SO_3R^a$, $C(=O)NH(CH_2)_3N^+(CH_3)_2-(CH_2)_3SO_3^-$, or -CN;

each R^4, independently, is H, alkyl, halo, or haloalkyl;

each R^5, independently, is H or alkyl;

each R^6, independently, is alkyl or aryl;

each R^7, independently, is alkyl;

each R^a is e^-, H, or a cation;

n is 0, 1, 2, 3, or 4;

m is 0, 1, 2, or 3;

x is greater than 0 and no greater than 1;

y is no greater than 1; and

z is from 0 to 0.5;

wherein x + y + z = 1, provided that x and z are not simultaneously 0.

19. The method of anyone of claims 16, 17, or 18, wherein said conducting polymer is PEDOT, a polyaniline, a polythiophene, or a combination thereof.

20. The method of anyone of claims 16, or 17-19, wherein said composition further comprises at least one of:

a metal oxide nano powder;

a carbon material selected from graphene oxide, graphitized carbon, graphite particles, carbon nanotubes, and carbon nanoparticles, or a combination thereof; and

a binder selected from PVDF, CMC, PTFE, PEO and poly(vinyl alcohol), or a combination thereof.

21. The method of claim 16, wherein said crosslinking uses a crosslinker comprising glutaraldehyde, (3-glycidyloxypropyl)trimethoxysilane, dithiobis(succinimidyl propionate), disuccinimidyl suberate, or any other bifunctional cross-linking unit.

22. A method of producing an electrode, for use as a cathode, comprising:

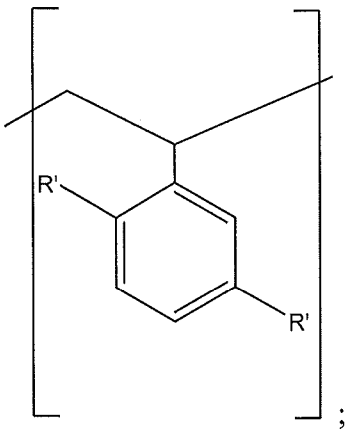
providing a composition containing a capacitive polymer, a conductive polymer, and a solvent; and

depositing said composition on a substrate;

wherein said capacitive polymer comprises an alkane chain backbone with pendant quinone unit; and

wherein said capacitive polymer and said conductive polymer form an interpenetrating network.

23. The method of claim 22, wherein said capacitive polymer is polyvinyl hydroquine having a structure of:



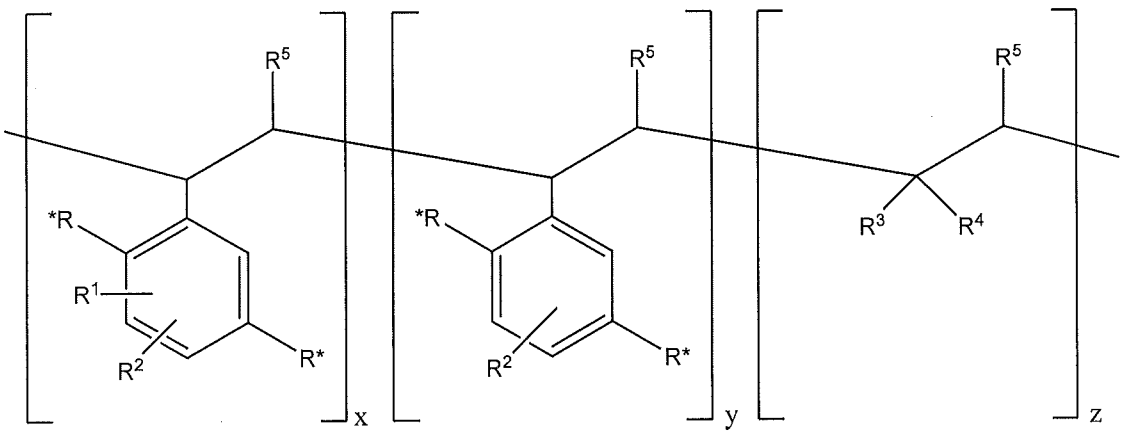
;

wherein:

each R', independently, is selected from the group consisting of OR^a or =O; and

each R^a is e^-, H, or a cation.

24. The method of claim 22, wherein said capacitive polymer has a structure of Formula (I)

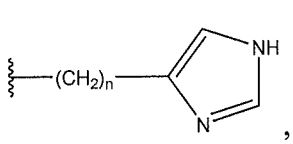


Formula (I)

wherein:

each R*, independently, is OR^a, =O , O-alkyl, $-OCO_2R^4$, -O-silyl group, or a protected hydroxyl group;

each R^1, independently, is $-SO_3R^a$, $-CO_2R^a$, haloalkyl, $-(CH_2)_n-N(R^6)_2$, $-(CH_2)_n-PO_3R^a$,



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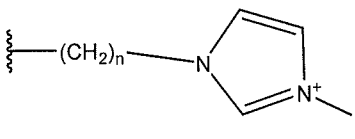
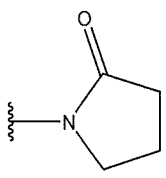


R^7, $-SO_2N(R^5)_2$, $-SO_2R^5$, $-N(SO_2R^6)_2$, $-N(SO_2CF_3)_2$, -CN, halo, or nitro;

each R^2, independently, is H, alkoxy, alkyl, halo, cyano, haloalkyl, or nitro;

each R^3, independently, is alkyl, aryl, $-(CH)_2CO_2R^5$, -OH, $-OC(=O)R^6$, $-C(=O)NHR^5$,

$-NHC(=O)CH_3$, $-(CH_2)_mSO_3R^a$, $-(CH_2)_m-PO_3R^a$, $-(CH_2)_mN^+(R^4)_3$,



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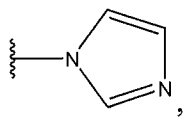
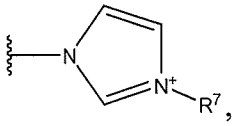
 ,  , -C(=O)NH-C(CH_3)$_2$-$CH_2SO_3R^a$, C(=O)NH$(CH_2)_3N^+(CH_3)_2$-$(CH_2)_3SO_3^-$, or -CN;

each R^4, independently, is H, alkyl, halo, or haloalkyl;

each R^5, independently, is H or alkyl;

each R^6, independently, is alkyl or aryl;

each R^7, independently, is alkyl;

each R^a is e^-, H, or a cation;

n is 0, 1, 2, 3, or 4;

m is 0, 1, 2, or 3;

x is greater than 0 and no greater than 1;

y is no greater than 1; and

z is from 0 to 0.5;

wherein x + y + z = 1, provided that x and z are not simultaneously 0.

25. The method of any one of claims 22-24, wherein said conducting polymer is PEDOT, a polyaniline, a polythiophene, or a combination thereof.

26. The method of any one of claims 22-25, wherein said composition further comprises at least one of:

a metal oxide nano powder;

a carbon material selected from graphene oxide, graphitized carbon, graphite particles, carbon nanotubes, and carbon nanoparticles, or a combination thereof; and

a binder selected from PVDF, CMC, PTFE, PEO and poly(vinyl alcohol), or a combination thereof.

27. The method of claim 25, further comprising crosslinking said capacitive polymer and said conductive polymer.

28. The method of claim 27, wherein said crosslinking uses a crosslinker comprising glutaraldehyde, (3-glycidyloxypropyl)trimethoxysilane, dithiobis(succinimidyl propionate), disuccinimidyl suberate, or any other bifunctional cross-linking unit.

29. The method of claim 22, wherein said substrate is a current collector.

30. The method of claim 22, wherein said substrate is a release film.

31. The method of claim 30, wherein said release film is at least one of a non-stick film or sacrificial layer.

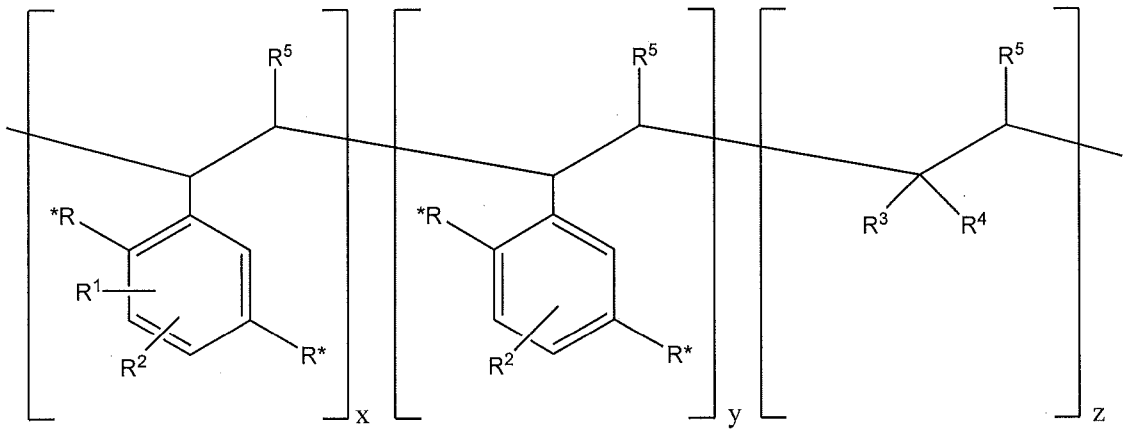
32. The method of claim 31, wherein said non-stick film comprises a TFE polymer, a CTFE polymer, an ETFE polymer, or an ECTFE polymer.

33. The method of claim 22, further comprising removing the solvent.

34. The method of claim 33, wherein said removing uses evaporation.

35. The method of claim 34, wherein said solvent is water.

36. A polymer of formula (I):

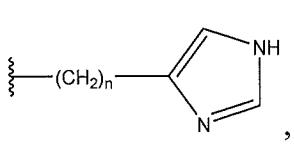


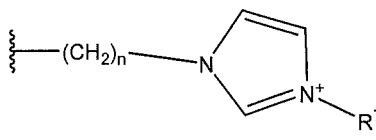
(I)

wherein:

each R*, independently, is OR^a, =O , O-alkyl, $-OCO_2R^4$, -O-silyl group, or a protected hydroxyl group;

each R^1, independently, is $-SO_3R^a$, $-CO_2R^a$, haloalkyl, $-(CH_2)_n-N(R^6)_2$, $-(CH_2)_n-PO_3R^a$,

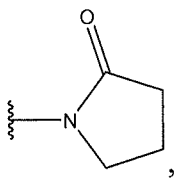


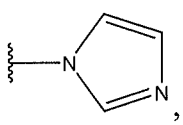


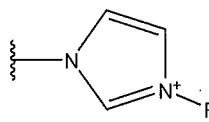
$-SO_2N(R^5)_2$, $-SO_2R^5$, $-N(SO_2R^6)_2$, $-N(SO_2CF_3)_2$, -CN, halo, or nitro;

each R^2, independently, is H, alkoxy, alkyl, halo, cyano, haloalkyl, or nitro;

each R^3, independently, is alkyl, aryl, $-(CH)_2CO_2R^5$, -OH, $-OC(=O)R^6$, $-C(=O)NHR^5$, $-NHC(=O)CH_3$, $-(CH_2)_mSO_3R^a$, $-(CH_2)_m-PO_3R^a$, $-(CH_2)_mN^+(R^4)_3$,







$-C(=O)NH-C(CH_3)_2-CH_2SO_3R^a$, $-C(=O)NH(CH_2)_3N^+(CH_3)_2-(CH_2)_3SO_3^-$, or -CN;

each R^4, independently, is H, alkyl, halo, or haloalkyl;

each R^5, independently, is H or alkyl;

each R^6, independently, is alkyl or aryl;

each R^7, independently, is alkyl;

each R^a is e^-, H, or a cation;

n is 0, 1, 2, 3, or 4;

m is 0, 1, 2, or 3;

x is greater than 0 and no greater than 1;

y is no greater than 1; and

z is from 0 to 0.5;

wherein x + y + z = 1, provided that x and z are not simultaneously 0.

37. The polymer of claim 36, wherein x is no greater than 0.5 and z is no greater than 0.1.

38. The polymer of claim 37, wherein x is no greater than 0.2 and z is no greater than 0.1.

39. The polymer of any one of claims 36-38, wherein z is 0.

40. The polymer of any one of claims 36-39, wherein each R^1 is $-SO_3R^a$ and each R^2 is H.

41. The polymer of any one of claim 36-38, wherein R* is OR^a or =O.

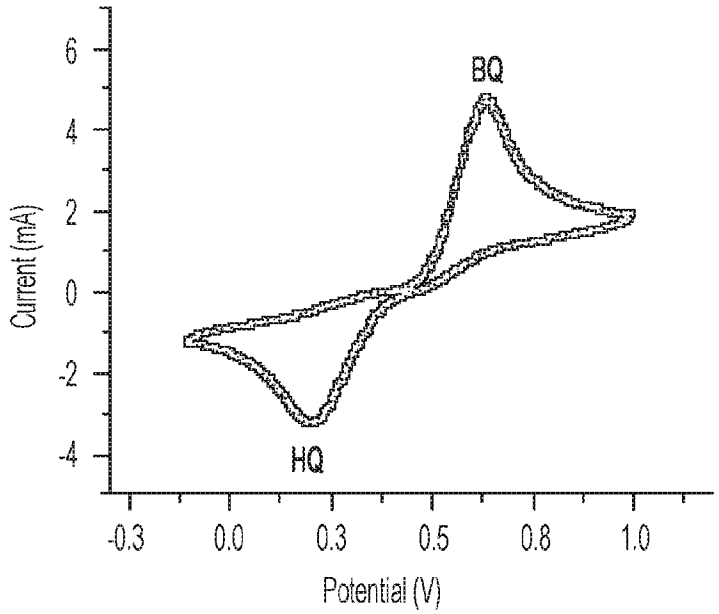


Figure 1

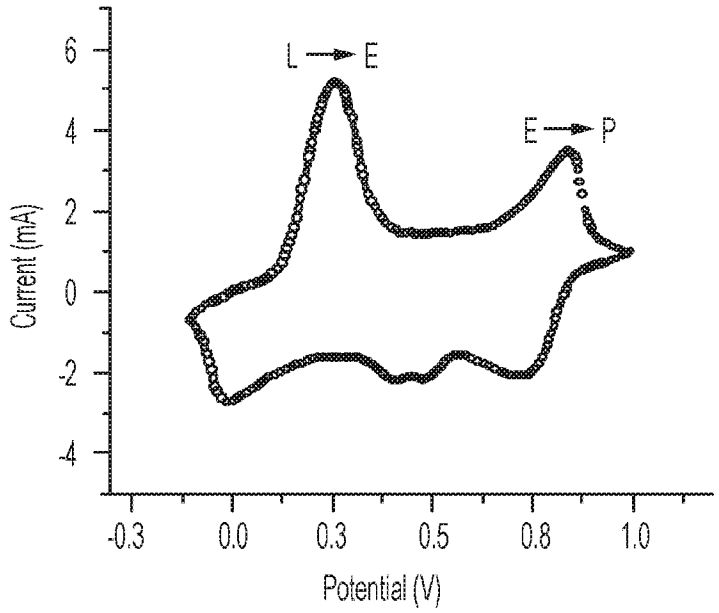


Figure 2

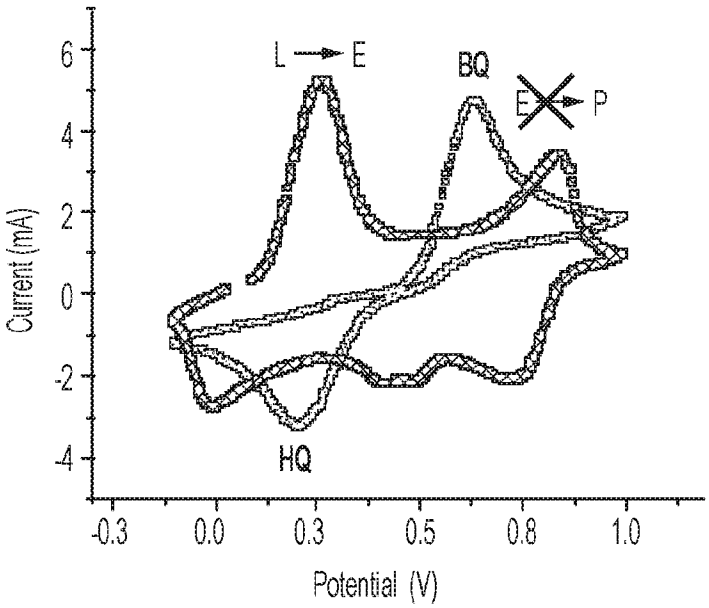


Figure 3

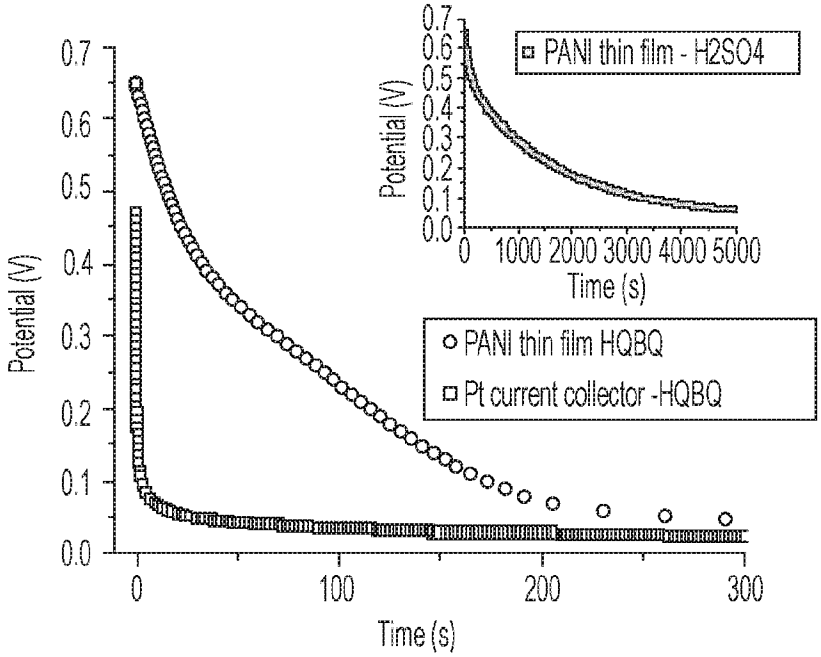


Figure 4

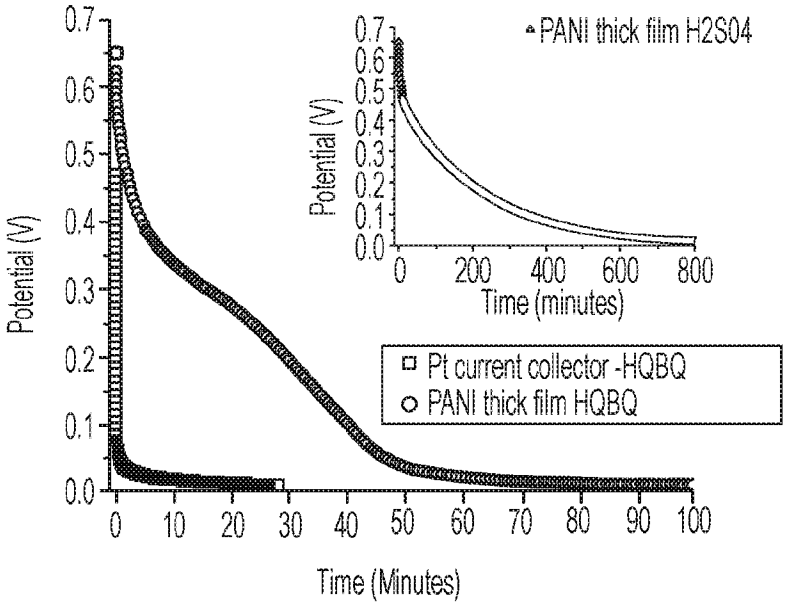


Figure 5

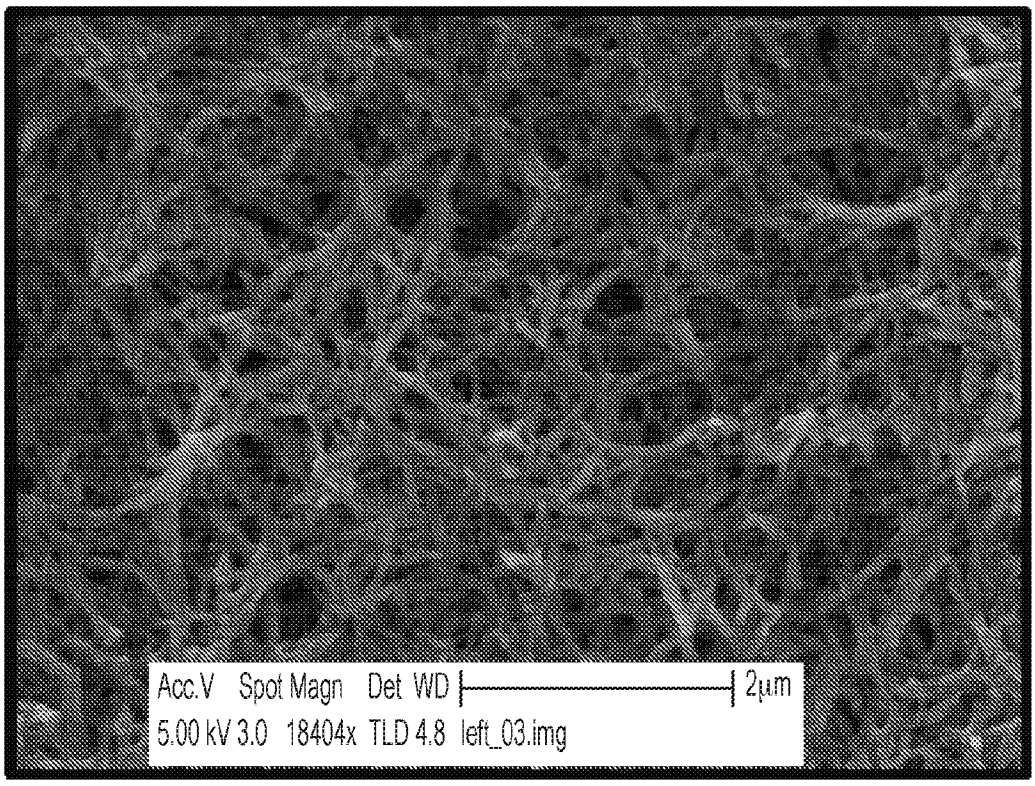


Figure 6

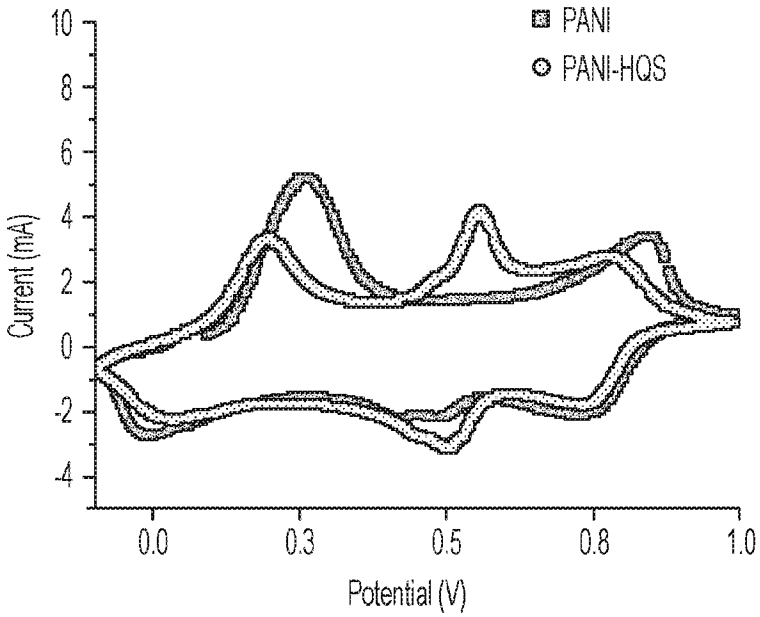


Figure 7

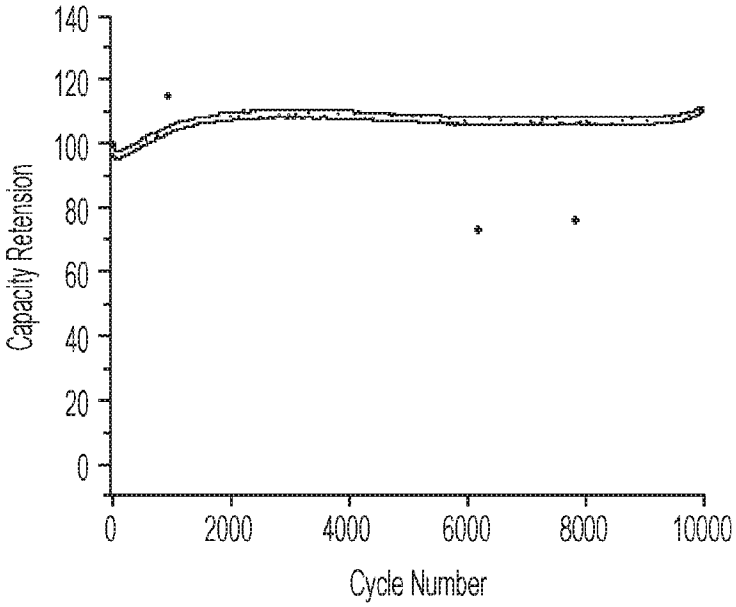


Figure 8

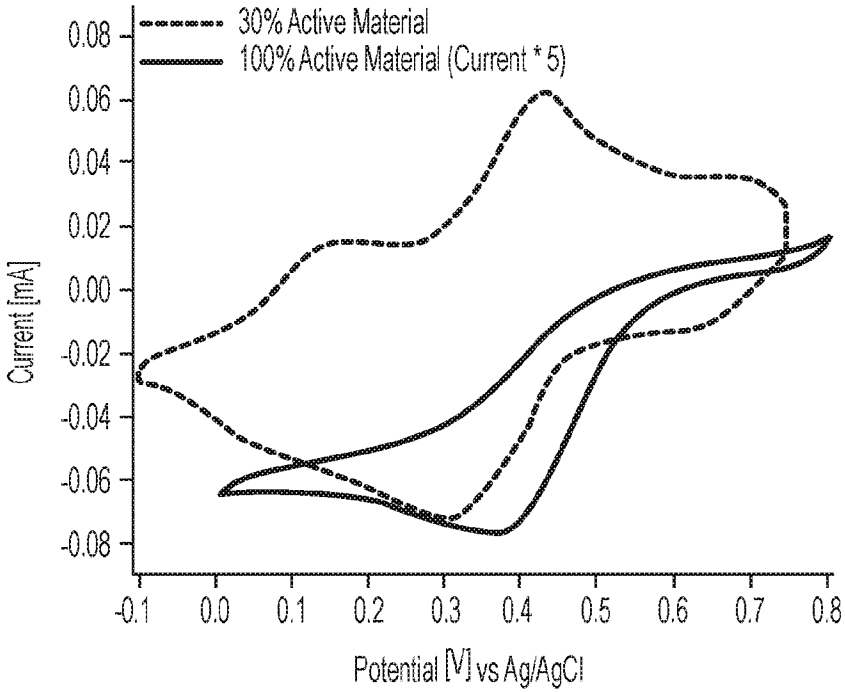


Figure 9

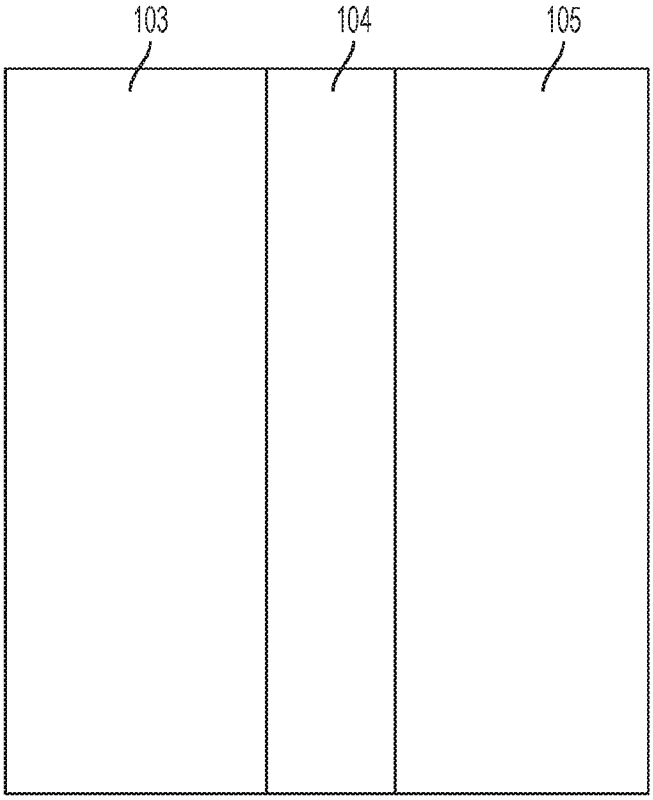


Figure 10

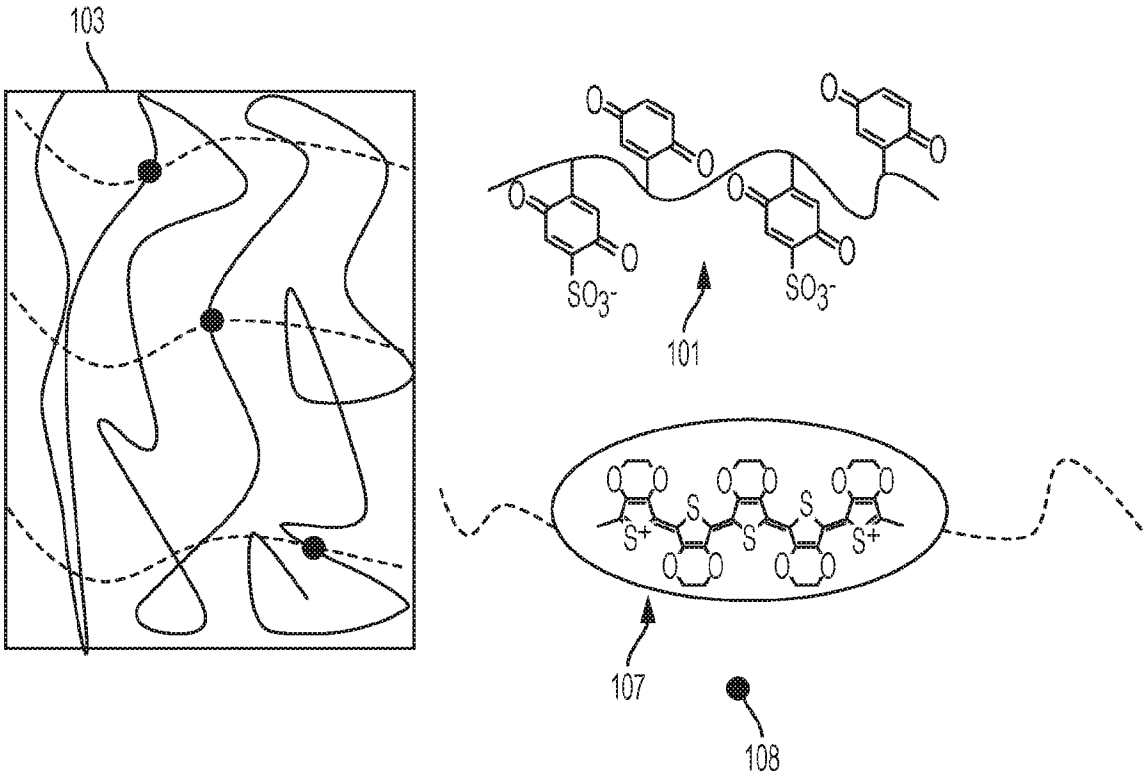


Figure 11

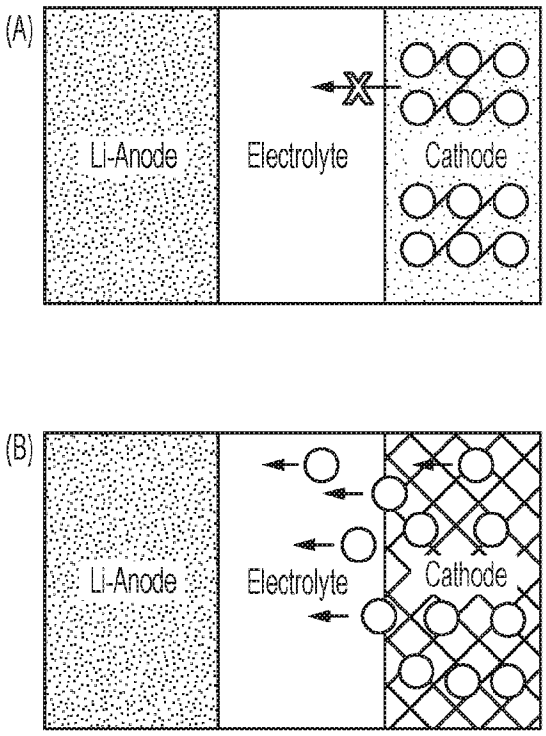
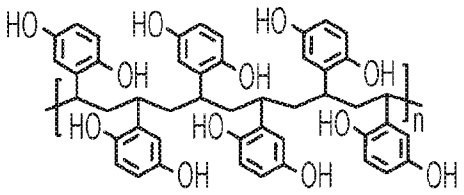


Figure 12A, 12B

Table 2.1 Characteristics of commercial Li-ion battery cathode materials

Material	Structure	Potential versus Li/Li^+,average V	Specific capacity, mAh/g	Specific energy, Wh/kg
$LiCoO_2$	Layered	3.9	140	546
$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA)	Layered	3.8	180-200	680-760
$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NMC)	Layered	3.8	160-170	610-650
$LiMn_2O_4$ and variants (LMO)	Spinel	4.1	100-120	410-492
$LiFePO_4$(LFP)	Olivine	3.45	150-170	518-587



392 mAh/g - 2.7V (Specific E ~*1060 Wh/kg*)

Figure 13

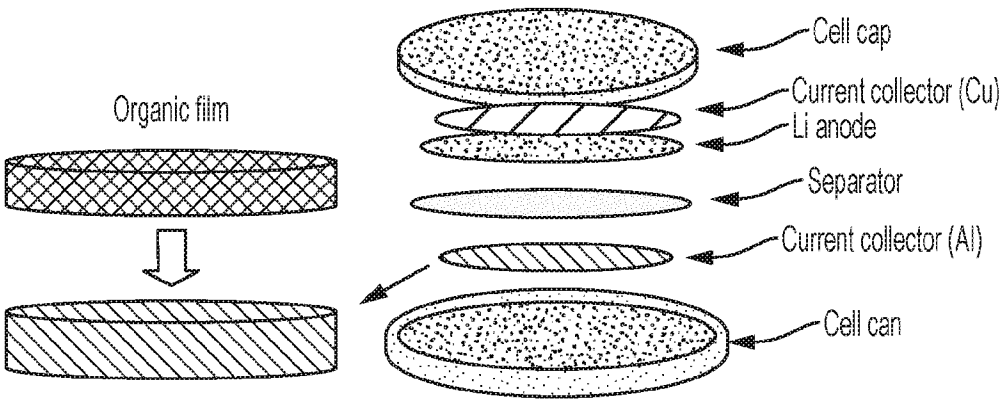


Figure 14

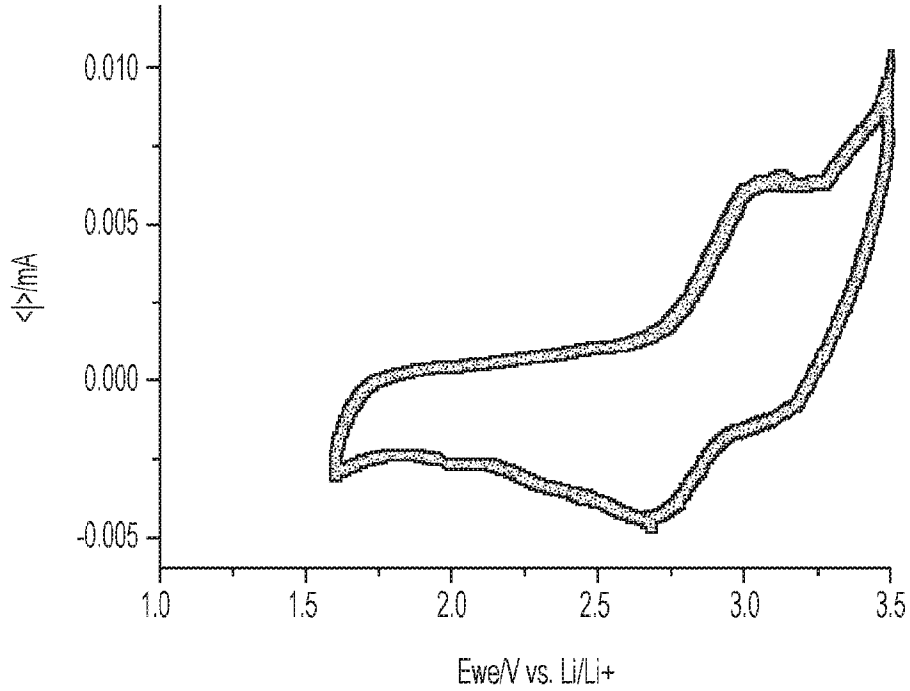


Figure 15

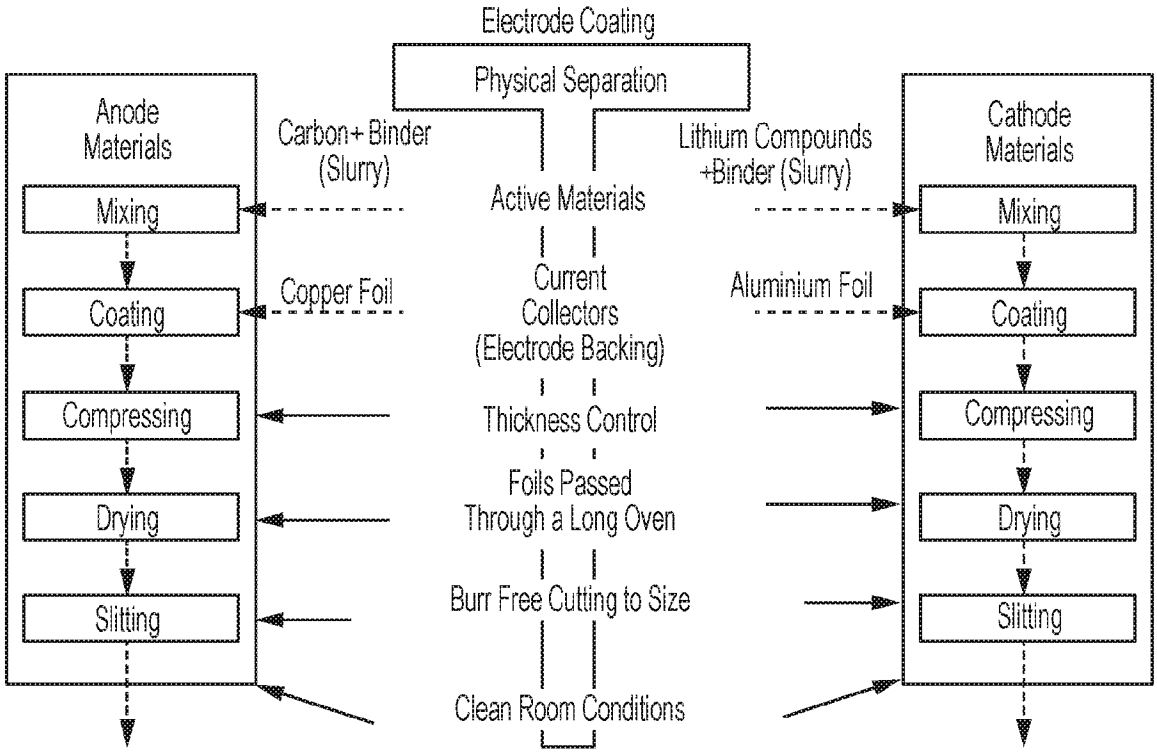


Figure 16

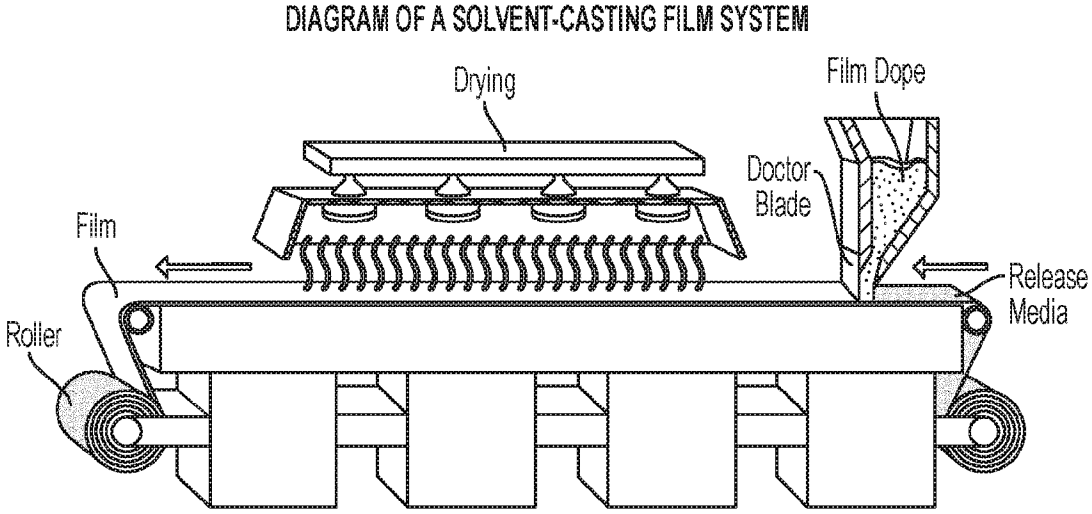


Figure 17

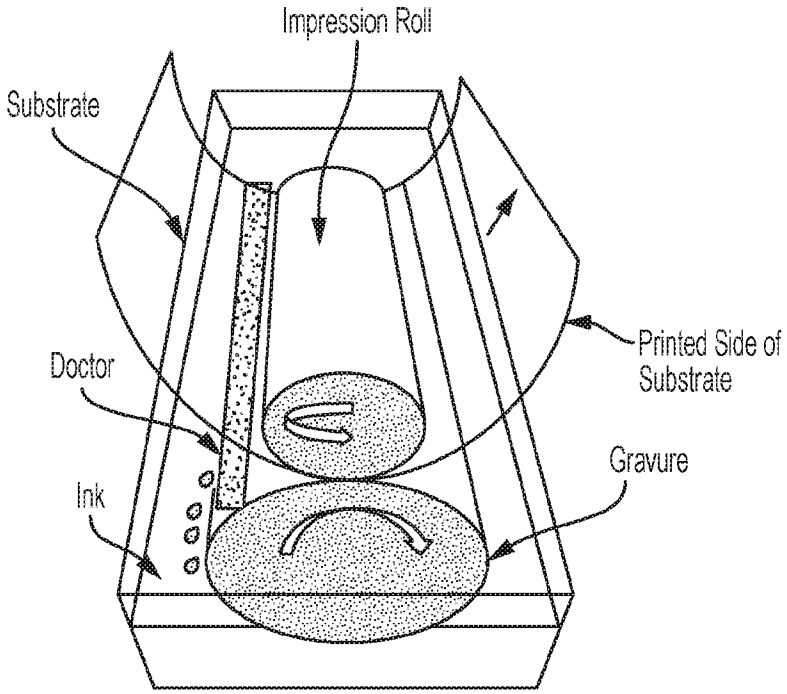


Figure 18

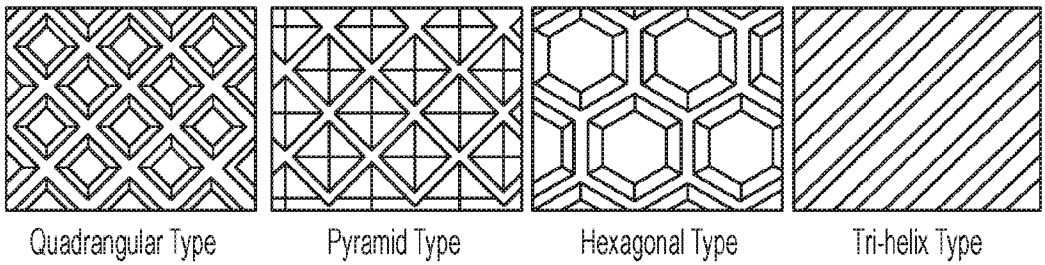


Figure 19

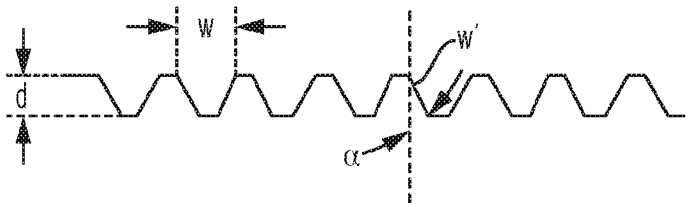


Figure 20

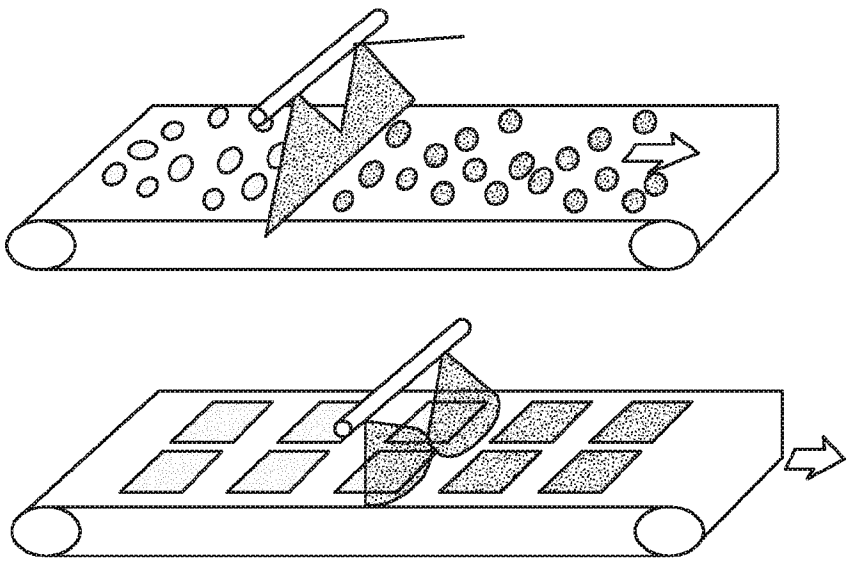


Figure 21

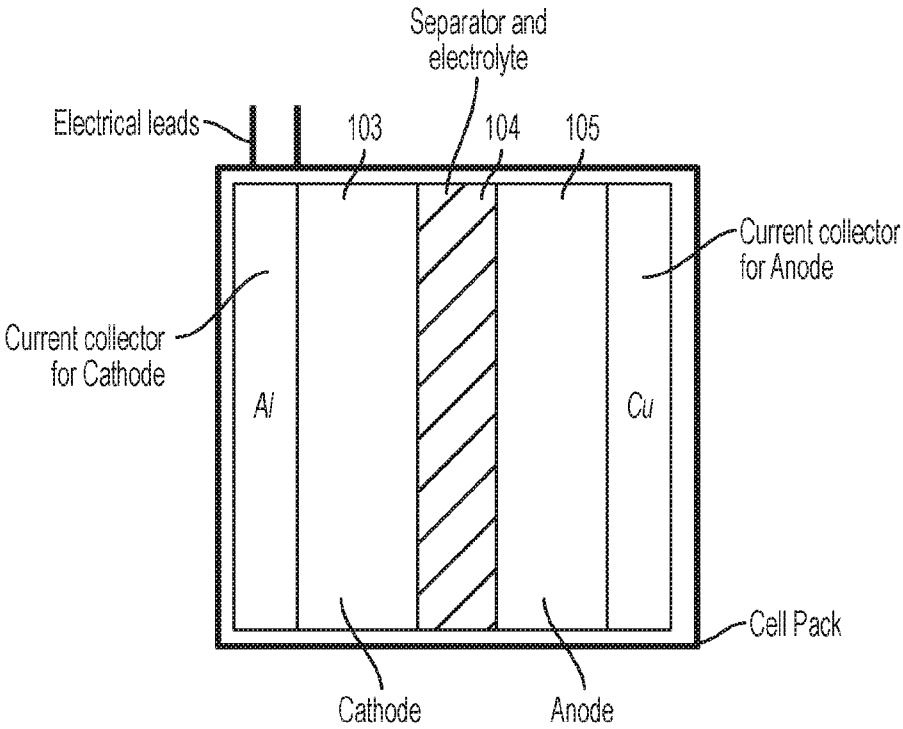


Figure 22

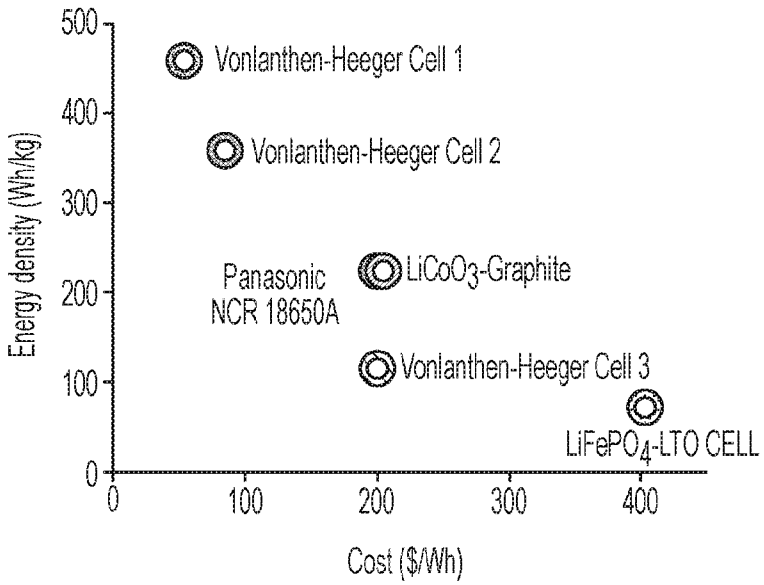


Figure 23

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/037682

A. CLASSIFICATION OF SUBJECT MATTER

H01G 11/48(2013.01)i, H01G 11/38(2013.01)i, H01M 4/60(2006.01)i, H01M 4/62(2006.01)i, H01M 4/13(2010.01)i, C08F 212/08(2006.01)i, C08L 25/06(2006.01)i

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)
H01G 11/48; C08L 65/00; C12Q 1/00; C08L 101/12; H01G 11/30; H01G 11/44; H01G 11/38; H01M 4/60; H01M 4/62; H01M 4/13; C08F 212/08; C08L 25/06

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: high capacity, cathode, anode, electrolyte, capacitive polymer, alkane chain backbone, pendant quinone unit, energy storage device

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2012-121417 A1 (WASEDA UNIVERSITY et al.) 13 September 2012 See abstract; claims 1, 7; paragraphs [0001], [0005]-[0009], [0059].	1-4,6-11,13-19,21-25,27-39,41
A	WO 2015-023974 A1 (THE REGENTS OF THE UNIVERSITY OF CALIFORNIA et al.) 19 February 2015 See the whole document.	1-4,6-11,13-19,21-25,27-39,41
A	WO 2009-148848 A1 (ABBOTT DIABETES CARE INC.) 10 December 2009 See abstract; claims 1, 7, 9, 15.	1-4,6-11,13-19,21-25,27-39,41
A	KARLSSON, C. et al., "Probing Polymer-Pendant Interactions in the Conducting Redox Polymer Poly(pyrrol-3-ylhydroquinone)", J. Phys. Chem., 2014, Vol.118, pages 23499-23508. See abstract; page 23499; scheme 1.	1-4,6-11,13-19,21-25,27-39,41
A	GOSWAMI, S. K. et al., "Linear electrochemical actuators with very large strains using carbon nanotube-redox gel composites", J. Mater. Chem. A, 2013, Vol. 1, pages 3415-3420. See figure 1; scheme 1.	1-4,6-11,13-19,21-25,27-39,41

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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

Date of the actual completion of the international search	Date of mailing of the international search report
12 October 2016 (12.10.2016)	**12 October 2016 (12.10.2016)**

Name and mailing address of the ISA/KR
International Application Division
Korean Intellectual Property Office
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/037682

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 5, 12, 20, 26, 40
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

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:

1. ☐ As all required addtional 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 an additional fees, this Authority did not invite payment of any 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.:

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.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2016/037682

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2012-121417 A1	13/09/2012	None	
WO 2015-023974 A1	19/02/2015	CA 2920365 A1	19/02/2015
		CN 105723482 A	29/06/2016
		EP 3033758 A1	22/06/2016
		KR 10-2016-0067837 A	14/06/2016
		US 2016-0196929 A1	07/07/2016
WO 2009-148848 A1	10/12/2009	US 2009-0294307 A1	03/12/2009
		US 2012-0078070 A1	29/03/2012