An electrochemical energy storage device (6) is described. The electrochemical energy storage device includes: (1) a polymer electrode having (A) an organic conjugated compound (12); and (B) an ionically conductive polymer electrolyte (14), wherein the organic conjugated compound and the ionically conductive polymer electrolyte form a bicontinuous interpenetrating network (10), in which the organic conjugated compound and the ionically conductive polymer electrolyte form distinct continuous phases and an average phase size of the organic conjugated compound in the bicontinuous interpenetrating network is in the order of nanometers; and (2) a separator that is electronically non-conductive and contacts the polymer electrode such that the separator facilitates the transport of ions to and from the polymer electrode. Another electrochemical energy storage device is also described. This electrochemical energy storage device includes a surfactant in the polymer electrode to form a bicontinuous interpenetrating network of nanometer scale phase size. Yet another electrochemical energy storage device is also described. This electrochemical energy storage device includes a conjugated compound having a side-chain that has an affinity to a polymer electrolyte and as a result, the conjugated compound and polymer electrolyte form a more compact bicontinuous interpenetrating network.
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POLYMERIC THIN-FILM REVERSIBLE ELECTROCHEMICAL CHARGE STORAGE DEVICES

BACKGROUND OF THE INVENTION

The present invention relates to electrochemical energy storage devices. More particularly, the present invention relates to electrochemical energy storage devices including at least one polymer electrode, which has a bicontinuous interpenetrating network of conjugated compounds and ionically conductive polymers.

Electrochemical storage devices, such as batteries, can be classified into either primary or secondary batteries. Primary batteries are not designed to be recharged and are not reusable after they have been fully discharged. Secondary batteries, however, are rechargeable after they have been fully discharged. One example of a commercially widely available primary battery is an alkaline battery, which typically includes a zinc anode of large surface area, a manganese dioxide cathode of high density and a potassium hydroxide electrolyte. Alkaline batteries have a nominal voltage of 1.5 V and operate over a wide temperature range (approximately -20 to 70 °C). Furthermore, they are capable of withstanding and functioning under severe operating conditions, such as mechanical shock, high pressure and the like.

The demand for rechargeable or secondary batteries of high energy density and specific energy has increased with the increasing demand for portable electronic equipment, e.g. cellular phones, laptop computers, consumer electronics, power tools, etc. In order to meet this demand, various types of rechargeable batteries have been developed including improved nickel-cadmium aqueous batteries, various formulations of aqueous nickel metal hydride batteries and non-aqueous rechargeable lithium batteries (hereinafter referred to as “Li-ion secondary batteries”). Nevertheless, all secondary battery chemistries are more expensive than primary battery chemistries. The Li-ion secondary battery chemistry is particularly expensive.

Nickel-cadmium aqueous batteries are the least expensive among the portable rechargeable battery chemistries mentioned above. A typical nickel-cadmium secondary battery (having a nominal voltage of about 1.2 V) includes a metallic cadmium sponge anode, a nickel hydrate (Ni(OH)₃) based cathode and an electrolyte, which may have an aqueous solution of potassium hydroxide (KOH). Some
advantages of this chemistry include long life (with up to 1500 charge discharge cycles), capability of high discharge rate, and quick charge times, for example. Nickel-cadmium batteries are particularly attractive in applications where low battery cost is of paramount importance and that require high discharge rates, which are not provided by other chemistries. Unfortunately, the use of cadmium in the nickel-cadmium chemistry is a growing environmental concern.

Nickel metal hydride is a rapidly growing alternative secondary battery chemistry. The primary difference between the nickel-cadmium battery chemistry and nickel metal hydride battery chemistry is that in the nickel metal hydride chemistry, the active material in the cathode is a hydrogen absorbing metal alloy, which reversibly absorbs and releases hydrogen gas generated by the electrochemical discharge reaction. Upon absorption of hydrogen, the metal alloy becomes a metal hydride. The advantages of nickel metal hydride chemistry over nickel-cadmium chemistry are the provision of higher energy densities and lack of cadmium-related environmental problems, for example. Nickel metal hydride batteries are, however, more expensive than nickel-cadmium batteries and less expensive than Li-ion batteries.

Among the commercially available portable rechargeable battery chemistries, Li-ion provides the highest energy densities. A typical Li-ion cell consists of a lithiated cobalt oxide, lithiated nickel oxide or lithiated manganese oxide based composite cathode, a carbon-based anode, and a lithium ion liquid electrolyte. Lithium is the lightest and is the most electropositive alkali metal (charge capacity 3.86 Ah/g). Li-ion batteries have a long cycle life, provide a high cell voltage and are capable of functioning at a wide temperature range. Unfortunately, Li-ion battery chemistry is the most expensive of the portable rechargeable battery chemistries and is inappropriate for applications requiring rapid discharge. Furthermore, Li-ion batteries typically require electronic circuits to monitor the discharge history and prevent overcharging. This protective circuitry adds to the cost of manufacturing a battery. Further still, it is expensive to produce the high quality porous electrodes that are employed in the Li-ion battery.

Lithium-polymer (Li-polymer) battery chemistry, which is a modification of the Li-ion battery chemistry, is an emerging secondary battery chemistry for portable electronics. Li-polymer chemistry is similar to the Li-ion chemistry, except that a polymer or polymer or gel electrolyte, e.g., a poly(vinylidene fluoride) (PVDF) electrolyte containing lithium salt, is used in place of a liquid electrolyte. Li-polymer chemistry has been proposed as the chemistry of choice over Li-ion in portable
electronic applications because the Li-polymer battery can be processed into a thin sheet whereas Li-ion batteries require a container for holding the liquid electrolyte. Thin sheet processability and deformability are ideal for portable electronic applications where space is at a premium. The elimination of the liquid electrolyte may improve safety characteristics over Li-ion cells, which use an inflammable liquid electrolyte. Unfortunately, the Li-polymer batteries also suffer from some of the same drawbacks as the Li-ion battery mentioned above; e.g., added costs of overcharge monitoring circuits.

Note that the lithium metal anode is responsible for dendrite formation. In order to circumvent the dendrite formation in the Li-polymer battery mentioned above, Li-ion chemistries typically employ Li insertion compounds instead of Li metal as the anode material. In this case, dendrite formation is avoided as long as the potential between the two electrodes never reaches Li/Li⁺. Li insertion compounds are known to have open structures that are capable of accepting and releasing Li⁺ ions. By way of example, one such lithium insertion compound for the anode is Li₄C₁₅, which has a charge capacity for x=0.5 of about 0.186 Ah/g. Unfortunately, the performance of the cathode (e.g., lithiated cobalt oxide, lithiated nickel oxide or lithiated manganese oxide based composites) and anode materials is dependent on their morphology, which controls the ionic conductivity. Thus, in order to have a sufficiently high ionic conductivity in the presence of negligible bulk ionic diffusion, high quality porous electrodes are necessary. Consequently, even with the use of lithium insertion compounds, the drawbacks of significant costs associated with high quality porous electrodes and electronic circuitry for protection against overvoltage still persists.

The search for a commercially viable battery technology for portable electronic applications is leading to conductive polymer electrode technology, which is still very much in its infancy. The polymer electrode typically includes conjugated polymers, which are known like other polymers to undergo p-type doping with good reversibility. By way of example, typical upper limits for anion intercalation (p-type doping) of lower energy gap polymers (i.e. having an energy gap of approximately 2 eV) is about 0.25 electrons per basic conjugation unit and of higher energy gap polymers (i.e. having an energy gap higher than approximately 3 eV) is about 0.3 to about 0.5 electrons per basic conjugation unit. The typical upper limits for cation intercalation (n-type doping) are lower than the upper limits for anion intercalation mentioned above. Furthermore, the charge capacity of the conjugated polymers are lower than the corresponding theoretical values for Li metal and Li intercalation anodes mentioned above.
Bridgestone Lithium Polymer Button Cell (hereinafter referred to as "button cell"), available from Bridgestone Corporation of Tokyo, Japan, is one polymer electrode electrochemical device that is commercially available. It employs a LiAl (lithiated aluminum) anode, polyaniline cathode and a liquid electrolyte. It is a supercapacitor and therefore high charge capacity is not essential. The button cell, for example, has a nominal charge capacity of about 4 mAh and is designed for $>10^3$ shallow cycles at 1 mAh.

Unfortunately, the Bridgestone button cell fails to meet the power demands of most portable electronic equipment. The button cell is employed in a limited role as an electrical buffer in electronic circuitry. By way of example, in solar cells the button cell may function as a support cell when the main cell for energizing the circuit is inactive. Thus, the button cell fails to fully exploit the advantages of polymer-based systems to increase the energy density of the battery, which would make it suitable for portable electronic equipment applications.

Furthermore, the button cell has a polymer electrode that is made from electrochemically synthesized polyaniline, which is undesirable for large scale fabrication of electrodes. Further still, polyaniline film produced electrochemically is brittle and tends to break when subject to external force. Consequently, polyaniline electrode fails to lend itself to thin film processability.

What is therefore needed is a low cost battery chemistry that has performance comparable to commercially available chemistries and offers thin sheet processability and deformability.
SUMMARY OF THE INVENTION

The present invention provides polymer electrodes for electrochemical energy storage devices. The polymer electrodes include the following components: (a) a conjugated compound and (b) an ionically conductive polymer. Further, the polymer electrode has a bicontinuous interpenetrating network, in which the conjugated compound and the ionically conductive polymer form distinct continuous phases. At least one continuous phase in the bicontinuous interpenetrating network has an average phase size of less than about 1 micrometer. Preferably, the average diameter of a strand of the conjugated compound is between about 1 nanometer and about 1 micrometer. Further, the conjugated compound preferably has an energy gap that is at least about 1 eV and more preferably at least about 2 eV.

Preferably, the conjugated compound has a conjugation length that optimizes the energy gap and electronic conductivity of the electrode. To this end, the conjugated compound preferably has between about 2 and 12 successive basic conjugation units (e.g., phenyl or allyl groups). More preferably, the conjugated compound has between about 3 and 8 successive basic conjugation units.

In one embodiment, the conjugated compound includes a conjugated back-bone that is at least one of a substituted or an unsubstituted homopolymer, copolymer or oligomer having mer units selected from the group consisting of phenylene vinylene, phenylene, fluorene, quinoline, quinoxaline, acetylene, aniline, phenylene-2,6-benzobisthiazole, phenylene-2,6-benzobisoxazole, phenylene-2,6-benzimidazole, arylene, and arylene vinylene, and wherein the arylene is one of the following groups: naphthalene, anthracene, furylene, thiénylene, pyrrole, oxadiazole, selenylene and isothenaphthene. In some cases, the conjugated compound also includes side-chains including at least one segment containing mer units selected from the group consisting of alkylene, acrylate, carbonate, styrene, ester, urethane, siloxane, phosphazene, amide, imide, itaconate, glutamate, p-phenylterephthalate, ethylene oxide, propylene oxide, oxymethylene, epichlorohydran, bis-(methoxyethoxyethoxy) phosphazene, oxetane, tetrahydrofuran, 1,3-dioxolane, ethylene imine, nitrile, ethylene succinate, ethylene sulfide, propylene sulfide, (oxyethylene) methacrylate, (oxyethylene) oxymethylene and derivatives of the mer units of the group.

In another embodiment, the conjugated compound includes a non-conjugated back-bone and conjugated side chains. In this case, the non-conjugated back-bone may include mer units selected from the group consisting of alkylene, acrylate, carbonate, styrene, ester, urethane, siloxane, phosphazene, amide, imide, itaconate,
glutamate, p-phenylterephthalate, ethylene oxide, propylene oxide, oxymethylene, epichlorohydran, bis-(methoxymethoxyethoxy) phosphazene, oxetane, tetrahydrofuran, 1,3-dioxolane, ethylene imine, ethylene succinate, ethylene sulfide, propylene sulfide, (oxyethylene) methacrylate, (oxyethylene) oxymethylene, (oxyethylene) cyclotrisphosphazene, (2-(4-carboxyhexafluorobutanoxyloxy) ethylmethacrylate and derivatives of the compounds of the group. Further, the conjugated side-chains may include a substituted or an unsubstituted homopolymer, copolymer or oligomer having mer units selected from the group consisting of phenylene vinylene, phenylene, fluorene, quinoline, quinoxaline, acetylene, aniline, phenylene-2,6-benzobisthiazole, phenylene-2,6-benzobisoxazole, phenylene-2,6-benzimidazole, arylene, and arylene vinylene, wherein arylene is one compound selected from the group consisting of naphthalene, anthracene, furylene, thiénylene, pyrrole, oxadiazole, selenylene or isothianaphthene.

In a preferred embodiment, the ionically conductive polymer has an ionic conductivity that is at least about 100 times greater than its electronic conductivity. It may be complexed with a salt to increase its ionic conductivity.

The ionically conductive polymer may include mer units selected from a group consisting of ethylene oxide, propylene oxide, oxymethylene, epichlorohydran, bis-(methoxymethoxyethoxy) phosphazene, oxetane, tetrahydrofuran, 1,3-dioxolane, ethylene imine, nitrile, ethylene succinate, ethylene sulfide, propylene sulfide, (oxyethylene) methacrylate, (oxyethylene) oxymethylene, (oxyethylene) cyclotrisphosphazene, (2-(4-carboxyhexafluorobutanoxyloxy) ethylmethacrylate and derivatives of the mer units of the group. In a specific embodiment, the ionically conductive polymer includes a polyelectrolyte and a counter ion. The polyelectrolyte includes a polymer or polymer component selected from the group consisting of (2-sulfonethyl methacrylates), (diallyldimethyl ammonium) chloride, (styrene sulfonate), nafion 117, (p-pheneylene terephthalamide sulfonate) salts, oligo (ethylene oxide) methacrylate-co-methacrylate salt and derivatives of the polymer or the copolymer of the group.

Examples of salts that may be used with the ionically conductive polymer include salts having cations selected from the group consisting of lithium, sodium, potassium, rubidium, cesium, aluminum, cobalt, silver, barium, calcium, copper, zinc, manganese, magnesium, chromium, ammonium, tetramethyl ammonium, tetraethyl ammonium, tetrapropyl ammonium, tetrabutyl ammonium, tetradecyl ammonium, tribenzyl-phenyl ammonium and tetrphenyl ammonium. The salts may also include anions selected from the group consisting of fluorine, chlorine, bromine, iodine,
perchlorate, bromate, nitrate, sulfate, phosphate, tetrafluoroborate, hexafluorophosphate, aluminum tetrachlorate, n-butyrate, trifluoromethane sulfonate, trifluoromethane sulfonamide, acetate, trifluoracetate, tetraphenylborate, toluene sulfonate, dodecylbenzene sulfonate, camphor sulfonate, picrate, salicylate, thiocyanate and benzoate.

Note that the ionically conductive polymer may have side chains that have an affinity for the conjugated compound such that the conjugated compound and the ionically conductive polymer are at least partially miscible. Examples of side-chains include those having at least one segment with mer units selected from the group consisting of methylene, ethylene, propylene, alkylene, acrylate, carbonate, styrene, ester, urethane, siloxane, phosphazene, amide, imide, itaconate, glutamate, p-phenylterephthalate, ethylene oxide, propylene oxide, oxymethylene, epichlorohydrin, bis-(methoxyethoxyethoxy) phosphazene, oxetane, tetrahydrofuran, 1,3-dioxolane, ethylene imine, ethylene succinate, ethylene sulfide, propylene sulfide, (oxyethylene) methacrylate, (oxyethylene) oxymethylene and derivatives of the merc units of the group.

In addition to the conjugated compound and the ionically conductive polymer (and possibly one or more of the additives described above), the electrodes of this invention may include a plasticizer. Preferably, the plasticizer is selected from the group consisting of ethylene oxide, polyethylene glycol, propylene oxide, oxymethylene, epichlorohydrin, bis-(methoxyethoxyethoxy) phosphazene, oxetane, tetrahydrofuran, 1,3-dioxolane, ethylene imine, ethylene succinate, ethylene sulfide, propylene sulfide, (oxyethylene) methacrylate, (oxyethylene) oxymethylene, (oxyethylene) cyclotrisphosphazene, (2-(4-carboxyhexafluorobutanoxyloxy) ethylmethacrylate), (2-sulfonethyl methacrylates), methylene, ethylene, propylene, alkylene, acrylate, carbonate, styrene, ester, urethane, siloxane, phosphazene, amide, imide, itaconate, glutamate, p-phenylterephthalate, tetramethyl ammonium, tetraethyl ammonium, tetrapropyl ammonium, tetrabutyl ammonium, tetradeoxy ammonium, tribenzyl-phenyl ammonium, tetraphenyl ammonium, perchlorate, bromate, nitrate, sulfate, phosphate, tetrafluoroborate, hexafluorophosphate, aluminum tetrachlorate, n-butyrate, trifluoromethane sulfonate, trifluoromethane sulfonamide, acetate, trifluoroacetate, tetraphenylborate, toluene sulfonate, dodecylbenzene sulfonate, camphor sulfonate, picrate, salicylate, thiocyanate, benzoate, crown ethers, dimethylphthalate, dibutylphthalate, 1,2,4-butanetriol trinitrate, pentabromo-diphenyl ether, arylphosphate, glycerine, sulfone amide, phosphate ester, benzoate ester and derivatives thereof.
Further, the polymer electrode may include a surfactant having a first moiety that has an affinity for the conjugated compound and a second moiety that has an affinity for the ionically conductive polymer such that the presence of the surfactant in the solution makes the conjugated compound and the ionically conductive polymer at least partially miscible. Examples of suitable surfactants include N,N-diethyldodecanamide, stearamide, N-dodecylpyrrolidinone, octylcyanooacetate, dodecanolactone and 2-tert-butylcyclohexanone.

In a further preferred embodiment, the polymer electrode includes carbon particles dispersed in the polymer electrode. The carbon particles have a concentration that is greater than or about equal to a percolation threshold concentration. This ensures that at least one electrically conductive pathway exists from one end to another end of the polymer electrode.

This invention also relates to electrochemical energy storage devices (e.g., secondary batteries) that include a polymer electrode as described above. In addition, such devices include a counterelectrode and a separator that is electronically non-conductive and contacts the polymer electrode in a manner allowing the transport of ions to and from the polymer electrode. The counterelectrode is preferably polymeric as described above, but may also be a metal electrode. Such devices may further include a current collector that is in electrical contact with the polymer electrode.

Preferably, the separator is a gel electrolyte that conducts ions to and from the polymer electrode and includes at least one of a polymer, copolymer and oligomer having mer units selected from the group consisting of substituted or unsubstituted vinylidene fluoride, urethane, ethylene oxide, propylene oxide, acrylonitrile, methylmethacrylate, alkylacrylate, acrylamide, vinyl acetate, vinylpyrrolidinone, tetraethylene glycol diacrylate, phosphazene and dimethylsiloxane. As noted above, preferably the counterelectrode is a polymer electrode, as described above. When the counterelectrode is a metal electrode, it preferably includes at least one material selected from the group consisting of alkali metals, alkali metal alloys, and alkali metal insertion compounds.

The present invention also provides methods of forming a polymer electrode for an electrochemical energy storage device. The method may be characterized by the following sequence: (a) combining a conjugated compound and an ionically conductive polymer to form an electrode mixture and (b) forming the polymer electrode of predefined dimensions from the electrode mixture. Preferably, the resulting polymer electrode has a bicontinuous interpenetrating network, in which the conjugated compound and the ionically conductive polymer form distinct continuous
phases and wherein at least one continuous phase in the bicontinuous interpenetrating network has an average phase size as described above.

“Combining the conjugated compound and the ionically conductive polymer” may include preparing in a common solvent or solvent mixture a solution of the conjugated compound and the ionically conductive polymer. In a preferred embodiment, the solvent or solvent mixture includes at least one material selected from the group consisting of propylene carbonate, ethylene carbonate, diethyl carbonate, dimethylcarbonate, dipropylcarbonate, dimethylsulfoxide, acetonitrile, dimethoxyethane, tetrahydrofuran, n-methyl-2-pyrrolidinone, chlorobenzene, N,N-dimethyl formamide, chloroform, ortho-dichlorobenzene (ODCB), γ-butyrolactone, poly(ethylene glycol), dibutyl phthalate, dioctyl phthalate and derivatives of the group of the materials.

The solution may further include one or more additives such as a surfactant and/or a plasticizer. The surfactant will have a first moiety that has an affinity for the conjugated compound and a second moiety that has an affinity for the ionically conductive polymer such that the presence of the surfactant in the solution makes the conjugated compound and the ionically conductive polymer at least partially miscible.

The process may further involve (i) casting the solution on a substrate and (ii) removing the solvent or solvent mixture to form the polymer electrode on the substrate. The casting may include casting on a current collector the solution of the ionically conductive polymer and the conjugated compound such that the current collector serves as the substrate. Further, the process may include dipping the current collector in a solution of the conjugated compound before the casting.

The methods of this invention may further comprise dispersing carbon particles in the polymer electrode in a concentration that is at least equal to the percolation threshold concentration, whereby at least one electrically conductive pathway forms from one end to another end of the polymer electrode.

This invention also pertains to methods of preparing electrochemical energy storage devices from a polymer electrode prepared as described above. Such devices may be prepared by (a) providing a separator layer that is electronically non-conductive and (b) assembling the separator layer, the polymer electrode, and a counter electrode (also preferably a polymer electrode) such that the separator facilitates the transport of ions to and from the polymer electrode. The separator layer is preferably formed by (i) casting a solution of gelling polymer, solvent, and salt to
form film; and (ii) evaporating at least a portion of the solvent. The method may further involve cross-linking the gelling polymer.

These and other features of the present invention will be described in more detail below in the detailed description of the invention and in conjunction with the following figure.
BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a side-sectional view of an electrochemical charge storage device, according to one embodiment of the present invention.

Figure 2 shows a side-sectional view of a portion of an electrode, according to one embodiment of the present invention, employed in the electrochemical storage device of Figure 1, that includes a bicontinuous interpenetrating network having a nanometer scale phase size.
DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

To achieve the foregoing, the present invention provides high performance, low-cost, flexible film polymeric electrochemical energy storage devices for portable electronics applications. In the following description, numerous specific details are set forth in order to provide a thorough understanding of the present invention. It will be apparent, however, to those skilled in the art, that the present invention may be practiced without some or all of the specific details. In other instances, well known process steps have not been described in detail in order to not unnecessarily obscure the invention.

It is well known in the electrochemical cell technology that the energy density of an electrochemical cell may be raised by increasing the stored charge density and the cell voltage. To this end, the present invention provides an electrochemical energy storage device including at least one polymer electrode having a bicontinuous interpenetrating network, in which an conjugated compound (typically an organic compound) and an ionically conductive polymer (usually a polymer electrolyte) are present in distinct continuous phases and the average phase size of the conjugated compound in the interpenetrating network is on the order of nanometers.

The bicontinuous interpenetrating network of an electrode of the present invention effectively drives up the stored charge density when the following advantages are realized in concert. By way of example, the three-dimensional bicontinuous interpenetrating network increases the conjugated compound/electrolyte interface area and thereby minimizes the effective distances through which ions diffuse during doping and dedoping of the conjugated compound.

As another example, a larger conjugated compound/polymer electrolyte interface also increases the volume of the conjugated compound exposed to the electrolyte for ion exchange. Hence, the maximum allowable doping concentration in the conjugated compound is increased. As yet another example, shorter effective distances for ion diffusion in the presence of a polymer electrolyte having a high ionic conductivity reduces the time required for doping the polymer electrode.

In order to increase the energy density of the electrochemical cell by increasing the cell voltage, the present invention employs conjugated polymers with the appropriate energy gap and appropriate levels of lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO).
As explained below, formation of the bicontinuous interpenetrating network, in accordance with one embodiment of the present invention, is facilitated by selecting an appropriate moiety or side-chain that is attached to either the backbone of the conjugated compound or the polymer electrolyte or both. Additionally, in this embodiment, additives, a surfactant, a plasticizer or a low molecular weight compound may be added to improve physical properties. By way of example, the addition of a surfactant to a mixture of conjugated compound and polymer electrolyte facilitates forming a more compact bicontinuous interpenetrating network. As another example, the addition of a plasticizer enhances the mechanical properties of the electrode having the bicontinuous interpenetrating network.

Note that at least one of a surfactant or a plasticizer or other low molecular weight compound may be added to facilitate the formation of the bicontinuous interpenetrating network having a nanometer scale phase size. In this embodiment, the side-chain attached to the back-bone of the conjugated compound need not be chemically compatible with the polymer electrolyte in the bicontinuous interpenetrating network. In fact, neither the conjugated compound nor the ionically conductive polymer necessarily need a side chain to achieve the small phase sizes of this invention.

As is explained below, the present invention fully exploits the processing advantages of a polymer-based system to yield an electrochemical energy storage device that provide energy densities that are high enough to be employed in portable electronic applications.

Figure 1 shows an electrochemical energy storage device 6, according to one embodiment of the present invention, which includes current collectors 1 and 5, electrodes 2 and 4 that are separated by polymer electrolyte separator 3.

Although electrochemical energy storage device 6 is an electrochemical battery, it should be borne in mind that the present invention applies to other devices, e.g., electrochemical capacitors, that operate via electrochemical energy storage. Preferably, however, electrochemical energy storage device 6 is an electrochemical battery that is capable of repeatedly discharging through an external load and recharging by an external energy source.

Current collectors 1 and 5 may be made from any suitable material and in any functional design. In keeping with the goal of high energy densities and fabrication ease, the current collectors are preferably thin films, which include at least one material selected from the group consisting of porous graphite, porous, highly doped
inorganic semiconductor, highly doped conjugated polymer or carbon particles dispersed in a non-conjugated polymer matrix, aluminum, silver, platinum, gold, palladium, tungsten, indium, zinc, copper, nickel, iron, lead, lead oxide, tin oxide, indium tin oxide, graphite, doped silicon, doped germanium, doped gallium arsenide, doped polyaniline, doped polypyrrole, doped polythiophene, and derivatives and mixtures thereof.

In one embodiment, both electrodes 2 and 4 are polymer electrodes that include the bicontinuous interpenetrating network having a nanometer scale phase size. In an alternative embodiment, however, electrode 2 is a polymer electrode that includes the bicontinuous interpenetrating network having a nanometer scale phase size and the counterelectrode, electrode 4, may include at least one material selected from the group consisting of alkali metals (e.g., lithium), lithium alloys, and lithium insertion compounds, and other active metals such as zinc and aluminum.

The polymer electrode of the present invention, in one embodiment, includes a conjugated compound that is not necessarily, but preferably, electrically conductive and a polymer that is ionically conductive to form the bicontinuous interpenetrating network, in which the conjugated compound and the polymer electrolyte form distinct continuous phases. Furthermore, the average phase size (shown in Figure 2 as “d” denoted by reference numeral 16) of the conjugated compound in the bicontinuous interpenetrating network is on the order of nanometers. Thus, the bicontinuous interpenetrating network is referred to as the “bicontinuous interpenetrating network having a nanometer scale phase size” or “bicontinuous interpenetrating network of nanometer scale” in the description of this invention.

A conjugated compound of the present invention is a conjugated polymer, for example. In one embodiment of the present invention, the conjugation is on the backbone, which may have substituted thereon at least one moiety or side chain that is chemically compatible to the polymer electrolyte in the bicontinuous interpenetrating network having nanometer scale phase size. The length of the conjugation in the conjugated polymer back-bone may be sufficiently long so that the conjugated portion of the back-bone imparts to the conjugated compound adequate electrical conductivity.

Note that while electronic conductivity scales with conjugation length, energy gap scales inversely with conjugation length. Generally, both high electronic conductivities and high energy gaps are desired. Depending upon the application and desired properties of an electrochemical device, these competing effects will have to be traded off. Generally, overall performance may be optimized by choosing
conjugated compounds having conjugation lengths that extend for greater than or equal to 2 basic conjugation units and up to 12 basic conjugation units. Preferably the conjugation length extends for between about 3 and 8 basic conjugation units. A basic conjugation unit is a chemical unit having delocalized pi electrons over three or more carbon atoms. Typically such units are aromatic or allyl groups (whether substituted or not). Specific examples include allyl groups, phenyl rings, thiophene rings, furan rings, pyrrole rings, and pyridine rings. A conjugation unit may correspond to a repeating mer unit (e.g., phenyl groups in PPP) or may not (e.g., fluorene groups in polyfluorene).

A conjugated compound having a conjugated back-bone may include substituted or unsubstituted homopolymer or copolymer having mer units selected from the group consisting of phenylene vinylene, phenylene, fluorene, quinoline, quinoxaline, acetylene, aniline, phenylene-2,6-benzobistiazole, phenylene-2,6-benzobisoxazole, phenylene-2,6-benzimidazole, arylene, and arylene vinylene, wherein arylene is naphthalene, anthracene, furylene, thiylene, pyrrole, oxadiazole, selenylene or isothianaphthene and mixtures thereof. The conjugated compound may also be an oligomer having a low molecular weight moiety with mer units selected from the group of mer units of homopolymers and copolymers mentioned above.

Alternatively, in another embodiment of the present invention, the conjugation is on the side-chain that is attached to a non conjugated back-bone. The back-bone may be comprised of mer units such as alkylene (e.g., methylene, ethylene, and/or propylene), acrylate, carbonate, styrene, ester, urethane, siloxane, phosphazene, amide, imide, nitrile, itaconate, glutamate, p-phenylterephthalate, ethylene oxide, propylene oxide, oxymethylene, epichlorohydran, bis-(methoxyethoxyethoxy) phosphazene, oxetane, tetrahydrofuran, 1,3-dioxolane, ethylene imine, ethylene succinate, ethylene sulfide, propylene sulfide, (oxyethylene) methacrylate, (oxyethylene) oxymethylene, (oxyethylene) cyclotrisphosphazene, (2-(4-carboxyhexafluorobutanoxyloxy) ethylmethacrylate) and their derivatives or any other polymer without pi-conjugation along its back-bone. The conjugated side-chains, in this embodiment, may be a segment comprised of mer units selected from the group of mer units of the conjugated back-bone mentioned above.

The organic conjugated compound of the present invention may also be a block copolymer or oligomer, in which the back-bone has conjugated and non-conjugated segments. The conjugated segments of the block copolymer may include mer units selected from the group of mer units of the conjugated polymer back-bone mentioned above. The non conjugated segments of the block copolymer may include
mer units selected from the group of mer units of the non conjugated back-bone listed above.

In order to maximize the energy density of the electrochemical energy storage device, it is preferable to have the ratio of conjugated compound to the total mass of the device as close to unity as practically possible. Consequently, it is desirable to maximize the thickness of the composite material comprising the interpenetrating network, without sacrificing ionic conductivity. Thus, in one embodiment, the present invention employs an ioneically conductive polymer that is complexed with a salt to form a polymer electrolyte with the necessary high ionic conductivity. The population of ionic species in the interpenetrating network of the present invention should be sufficiently high such that the conjugated compound phase is rendered highly electronically conductive upon completion of electrochemical doping. In a preferred embodiment, the ionic conductivity of the polymer electrolyte should be at least about 100 times greater than its electronic conductivity.

In one embodiment, the polymer electrolyte in the bicontinuous interpenetrating network having nanometer scale phase size, includes a side group or a segment or homopolymer or copolymer or a crosslinked network having mer units selected from the group consisting of ethylene oxide, propylene oxide, oxymethylene, epichlorohydran, bis-(methoxyethoxyethoxy) phosphazene, oxetane, tetrahydrofuran, 1,3-dioxolane, ethylene imine, nitrile, ethylene succinate, ethylene sulfide, propylene sulfide, (oxyethylene) methacrylate, (oxyethylene) oxymethylene, (oxyethylene) cyclotrisphosphazene, (2-(4-carboxyhexafluorobutanyl) ethylmethacrylate) and their derivatives.

In another embodiment, a polyelectrolyte (e.g., a single ion conductor) along with its counter ion serves as the polymer electrolyte. By way of example, such polyelectrolytes include a polymer or copolymer selected from the group consisting of (2-sulfonethyl methacrylates), (diallyldimethyl ammonium) chloride, (styrene sulfonate), nafion 117, (p-phenylene terephthalamide sulfonate) salts, oligo (ethylene oxide) methacrylate-co-methacrylate salt and derivatives thereof.

Furthermore, the counter ion may be selected from the group consisting lithium, sodium, potassium, rubidium, cesium, aluminum, cobalt, silver, barium, calcium, copper, zinc, manganese, magnesium, chromium, ammonium, tetramethyl ammonium, tetraethyl ammonium, tetrapropyl ammonium, tetrabutyl ammonium, tetradecyl ammonium, tribenzyl-phenyl ammonium, tetraphenyl ammonium, fluorine, chlorine, bromine, iodine, perchlorate, bromate, nitrate, sulfate, phosphate, tetrafluoroborate, hexafluorophosphate, aluminum tetrachlorate, n-butyrate,
trifluoromethane sulfonate, trifluoromethane sulfonamide, acetate, trifluoroacetate, tetraphenylborate, toluene sulfonate, dodecylbenzene sulfonate, camphor sulfonate, picrate, salicylate, thiocyanate and benzoate.

In the conjugated back-bone embodiment of the present invention, the attached side chains may be chosen so that the solubility of the conjugated compound in the ionically conductive polymer is enhanced. Representative side chains include at least one segment having mer units selected from the group consisting of alkylene (e.g., methylene, ethylene, and/or propylene), acrylate, carbonate, styrene, ester, urethane, siloxane, phosphazene, amide, imide, nitrile, itaconate, glutamate, p-phenyterephthalate, ethylene oxide, propylene oxide, oxymethylene, epichlorohydran, bis-(methoxyethoxyethoxy) phosphazene, oxetane, tetrahydrofuran, 1,3-dioxolane, ethylene imine, ethylene succinate, ethylene sulfide, propylene sulfide, (oxyethylene) methacrylate, (oxyethylene) oxymethylene and their derivatives.

In order to form a bicontinuous interpenetrating network of nanometer scale phase size, it is preferable to employ side chains that are chemically compatible to the polymer electrolyte. The phrase “the side chain is chemically compatible to the polymer electrolyte,” as used in connection with the description of this invention, means that the side chain has a segment that is chemically identical (or at least quite similar) to a segment in the polymer electrolyte. Obviously, the choice of a side chain depends on the chemical nature of the ionically conductive polymer in the bicontinuous interpenetrating network. By way of example, preferable side chains include ethylene oxide, propylene oxide, oxymethylene, epichlorohydran, bis-(methoxyethoxyethoxy) phosphazene, oxetane, tetrahydrofuran, 1,3-dioxolane, ethylene imine, nitrile, ethylene succinate, ethylene sulfide, propylene sulfide, (oxyethylene) methacrylate, (oxyethylene) oxymethylene and their derivatives.

The electrode of the present invention may also include a salt made of cations and anions. Cations in the salt may be selected from the group consisting of lithium, sodium, potassium, rubidium, cesium, aluminum, cobalt, silver, barium, calcium, copper, zinc, manganese, magnesium, chromium, ammonium, tetramethyl ammonium, tetraethyl ammonium, tetrapropyl ammonium, tetrabutyl ammonium, tetradecyl ammonium, tribenzyl-phenyl ammonium, tetraphenyl ammonium and mixtures thereof. Anions in the salt may be selected from the group consisting of fluorine, chlorine, bromine, iodine, perchlorate, bromate, nitrate, sulfate, phosphate, tetrafluoroborate, hexafluorophosphate, aluminum tetrachlorate, n-butyrate, trifluoromethane sulfonate, trifluoromethane sulfonamide, acetate, trifluoroacetate,
tetraphenylborate, toluene sulfonate, dodecylbenzene sulfonate, camphor sulfonate, picrate, salicylate, thiocyanate and benzoate and mixtures thereof.

In order to minimize power loss due to self-discharge, the conjugated compound/polymer electrolyte interpenetrating network, which provides an electron conduction pathway, is interrupted by a separator 3 containing no electron conductors or semiconductors. The electronic conductivity of separator 3 is preferably as small as possible because electronic conduction in the separator causes an internal short circuit.

In one embodiment, separator 3 is a gel electrolyte rather than a liquid electrolyte. Liquid electrolytes are undesired to serve as separators because it is necessary to hold the liquid in a can. Polymer gel electrolytes, in contrast, do not have such constraints and lend the electrochemical energy storage device of the present invention to thin film processability. Furthermore, in order to optimize ionic transport in a high performance electrochemical energy storage device, gel electrolytes can have a higher ionic conductivity (e.g., approximately $10^3$ S/cm) than the polymer electrolytes.

The gel separator may be at least one of a polymer, copolymer and oligomer having mer units selected from the group consisting of substituted and unsubstituted vinyldene fluoride, urethane, ethylene oxide, propylene oxide, acrylonitrile, methylymethacrylate, alkylacrylate, acrylamide, vinyl acetate, vinylpyrrolidinone, tetraethylene glycol diacrylate, dimethylsiloxane, etc.

In one embodiment, separator 3 includes in its gelling solution (as explained later) at least one solvent selected from the group consisting of propylene carbonate, ethylene carbonate, diethyl carbonate, dimethylcarbonate, dipropylcarbonate, dimethylsulfoxide, acetonitrile, dimethoxyethane, tetrahydrofuran, n-methyl-2-pyrrolidinone, chlorobenzene, ortho-dichlorobenzene (ODCB), gamma-butyrolactone, poly(ethylene glycol), dibutyl phthalate, dioctyl phthalate and their derivatives. In another embodiment, separator 3 is a blend of common polymers that enhances the mechanical strength of the separator. By way of example, blend may include at least one inert polymer material selected from the group consisting of polyethylene, polypropylene, polytetrafluoroethylene, polystyrene, polyethylene terephthalate and nylon. In this embodiment, the various polymers may be held together by a bonding paste that includes at least one gelling polymer selected from the group consisting polyvinylidene fluoride (PVDF), polyurethane, polyethylene oxide, polypropylene oxide, polyacrylonitrile, polymethylmethacrylate, polyalkylacrylate, polyacrylamide, polyvinyl acetate, polyvinylpyrrolidinone, polytetraethylene glycol diacrylate, and
polydimethylsiloxane. The bonding paste may alternatively be a copolymer that includes a combination of gelling polymers mentioned above.

The thickness of the electrode(s) having the bicontinuous interpenetrating network, current collectors 1 and 5 and separator 3 may be of any appropriate thickness. In one embodiment, however, the thickness of the electrode having the bicontinuous interpenetrating network is between about 0.1 micrometer and about 10,000 micrometer, the separator 3 is between about 0.02 micrometer and about 100 micrometer and the current collectors 1 and 5 is between about 0.02 micrometer and about 100 micrometer.

The present invention recognizes that engineering a high cell voltage contributes to the requisite high energy density for commercial portable electronic applications. While intending not to be bound by theory, it is believed that the cell voltage of the electrochemical energy storage device is dependent on the energy gap between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) levels of the conjugated polymer. A twisted conjugated polymer back-bone is expected to have a higher energy gap than a planar conjugated polymer back-bone. Consequently, it is preferable to employ, in the interpenetrating network of the present invention, a conjugated polymer having an energy gap that is as large as possible without sacrificing electrochemical stability. More preferably, the energy gap of the conjugated polymer is at least about 1 eV, and even more preferably the energy gap is more than about 2 eV. By way of example, conjugated polymers falling within these classes include poly(1,4-phenylene) (PPP), poly(1,4-phenylene vinylene) (PPV), polyfluorenes (PF), polypyrrole, polyaniline and their derivatives.

Unsubstituted conjugated polymer chains are insoluble in many solvents. Those skilled in the art will recognize that it is difficult to make admixed polymer blends, if one of the polymer components is insoluble. The present invention recognizes that the conjugated polymer/polymeric electrolyte interpenetrating network having a phase size of nanometer scale is formed by judiciously choosing components or additives in a solution of conjugated compound and polymer electrolyte that render the conjugated polymer partially miscible in the polymer electrolyte solution. It is important to bear in mind that insoluble conjugated compounds may not yield nanometer scale interpenetrating network with nanometer scale phase sizes.

It is worthwhile to note that conjugated polymers selected in the present invention effectively combine the optical and electronic properties of conventional inorganic semiconductors, such as found in light emitting diodes, photovoltaic cells, and lasers, with the processing advantages and mechanical properties of polymers.
Conjugated polymers are electronic semiconductors in their undoped, neutral state and have the capability to undergo completely reversible p-type and n-type electrochemical doping. Electrochemically doped conjugated polymers have high electrical conductivities. This means that electrochemistry can be used to switch conjugated polymers between their semiconducting and conducting states. Thus, the conjugated polymers of the present invention are such that are able to undergo multiple doping and dedoping cycles with high charge capacity and good chemical stability.

The present invention also recognizes that the use of conjugated polymer technology for reversible charge storage is limited by the transport of ions in the conjugated compound, which is a poor ion conductor. Thus, the present invention employs at least one electrode having the bicontinuous interpenetrating network having a nanometer scale phase size, which network reduces the distance traveled by the ions in the conjugated compound phase. As will be explained later, during discharging or recharging of the electrochemical energy storage device of the present invention, the average distance traveled by the ions in the conjugated compound phase of the bicontinuous interpenetrating network of nanometer scale phase size will be equal to the diameter of the conjugated compound strand.

Figure 2 shows a representation of a bicontinuous interpenetrating network, according to one embodiment of the present invention, of nanometer scale phase size, in which a strand of conjugated compound 12 and polymer electrolyte 14 are present as distinct continuous phases. Each strand of conjugated compound 12 may include one or more fibrils of the conjugated compound. A diameter 16 (labeled “d” in Figure 2) of a conjugated compound strand represents an average diameter of the plurality of strands 12 in bicontinuous interpenetrating network 10. Diameter 16 also represents the average phase size of the conjugated compound 12 in bicontinuous interpenetrating network 10. As mentioned before, diameter 16 is the average maximum distance traveled by an ion during charging and discharging of the electrochemical energy storage device. The average phase size of the conjugated compound in the bicontinuous interpenetrating network of nanometer scale phase size is generally between about 1 nanometer and about 1 micrometer and preferably between about 20 and about 500 nanometers. Those skilled in the art will recognize that the phase size of the conjugated compound strand may be determined using a scanning electron microscope (SEM), for example.

A small phase size in bicontinuous interpenetrating network 10 reduces the detrimental effect of isolated polymer islands. In a “bulk” sample of conjugated
compound where the phase size of the conjugated compound is substantially larger than the diameter of conjugated compound fibrils, the full reversibility of electrochemical doping and dedoping is limited by the presence of isolated charged islands surrounded by discharged areas. In bicontinuous interpenetrating network 10 of Figure 2, however, this problem is minimized because the polymer electrolyte having a high ionic conductivity is always reasonably close to the ionic species source and sink, i.e. the conjugated compound.

The ability to achieve reversible electrochemical doping is a unique advantage of the present invention. Inorganic semiconductors such as Si and the Group III-V alloys can be doped by the irreversible incorporation of electron deficient or electron rich elements into the lattice, but not electrochemically. Non-conjugated polymers such as polyethylene, polystyrene, polyethylene oxide (PEO), polycarbonate (PC), poly(vinylidene fluoride) (PVDF), and polyacrylonitrile, are electronic insulators and cannot undergo electrochemical doping to attain high electrical conductivities.

In one embodiment, the conjugated compound of the present invention has pendant solubilizing, flexible side chains, which render the conjugated compound partially miscible in the polymer electrolyte and facilitate forming the interpenetrating network of nanometer scale phase size shown in Figure 2. The side-chains of the conjugated compound in this embodiment have an affinity for the polymer electrolyte in the bicontinuous interpenetrating network.

The term “affinity,” as used in connection with the description of this invention, refers to the similarity in molecular structures of the conjugated polymer side chain and the polymer electrolyte. They are chemically compatible and exhibit an affinity for each other.

Affinity may be attained in this invention by, for example, employing similar molecular structures in the side-chains of the conjugated compound and the polymer electrolyte. As a result, entropy of mixing of the two phases is lowered and the length scale of the interpenetrating network features will be more compact. This is also referred to as chemical compatibility of the conjugated polymer to the polymer electrolyte. When the conjugated compound is rendered partially miscible in the polymer electrolyte, in this manner, there is a higher degree of interpenetration between the conjugated compound and the polymer electrolyte and a larger surface area of the conjugated compound is exposed to the polymer electrolyte in the interpenetrating network. As a result, there is a reduction in the average phase size of the conjugated compound. By thermodynamic considerations, the entropy of mixing the conjugated compound and the polymer electrolyte can become negligibly small.
and greater than zero and phase segregation occurs to form the bicontinuous interpenetrating network.

Alternatively, in an another embodiment, the pendant solubilizing, flexible side chains are attached to the polymer electrolyte, instead of the conjugated compound as described above, to render the conjugated compound partially miscible in the polymer electrolyte and facilitate forming the interpenetrating network of nanometer scale phase size shown in Figure 2. Thus, in the embodiment, the side-chains of the polymer electrolyte have an affinity for the conjugated compound in the bicontinuous interpenetrating network.

In the above-described embodiments, the concentration of each phase, i.e. the conjugated compound or the polymer electrolyte, in a blend of the conjugated compound and the polymer electrolyte is near to or above its percolation threshold. Those skilled in the art will recognize that concentrations above the percolation threshold ensure that there is at least one conductive pathway from one side of the interpenetrating network to another. For example, in order to obtain a high electronic conductivity, the concentration of the electronically conductive phase in the blend should exceed the percolation threshold concentration for that material in the blend.

Generally, the percolation threshold concentration, in connection with the description of this invention, refers to the concentration of one phase in the blend of the conjugated compound and the polymer electrolyte above which there is a possibility of finding a conducting pathway from one side of the sample to another. In practical terms, concentrations of a phase in the interpenetrating network above the percolation threshold may be accomplished by measuring the conductivity (electronic or ionic) of the interpenetrating network as a function of the concentration of each phase, identifying percolation thresholds and making blends of the two phases that have concentrations above those thresholds. The appropriate concentrations of a phase in a blend of two compounds may generally be more than about 80% of the percolation threshold concentration and preferably be more than about 100% of the percolation threshold concentration.

The blend of conjugated compound and the polymer electrolyte may include a plasticizer to enhance the mechanical properties of the bicontinuous interpenetrating network. The blend may additionally or alternatively also include a low molecular weight compound that has the appropriate miscibility in the conjugated compound and polymer electrolyte matrix to enhance the ionic conductivity of the bicontinuous interpenetrating network.
 Appropriately selected side-chains on the conjugated compound that are ionic or contain ion-solvating moieties may also enhance ionic transport to the conjugated compound. Conjugated compounds with ionic side chains are also called conjugated polyelectrolytes or rigid-rod polyelectrolytes and depending upon the choice of pendant ionic moiety, the conjugated compound may be water-soluble. Solubility of the conjugated compound in water allows fabrication of an electrochemical energy storage device without the use of organic solvents. In addition to water solubility, conjugated polyelectrolytes show good electrical conductivity (0.01 - 10 S cm\(^{-1}\)) as cast films and exhibit a novel feature called self-doping. Upon p-type doping (oxidation) in a conventional conjugated compound, in which an electron is taken away from the compound, an anion (available from the polymer electrolyte phase) is incorporated to preserve electrical neutrality. In a self-doped polymer, an electron is taken away and a cation is ejected from the ionic side chain, leaving behind the attached anion.

By way of example, a conjugated compound of the present invention is poly (9,9-bis (3,6-dioxahexyl)-fluorene-2,7-diyl] (BDOH-PF), which has a poly (1,4-phenylene) main chain that is capable of transporting electrons and holes, while the bis (3,6-dioxahexyl) side groups function to solvate ions and promote ion transport as required for high performance electrodes.

As explained above, in one embodiment, the interpenetrating network of the present invention is formed by selecting the appropriate side-chain. In an alternative embodiment, however, the interpenetrating network of the present invention is formed by admixing an additive, e.g., a surfactant, with the blend of the conjugated compound and polymer electrolyte. In this embodiment, the additive includes a first moiety that has an affinity for the conductive conjugated compound and a second moiety that has an affinity for the polymer electrolyte. As a result, the presence of the additive in a solution that includes the conjugated compound and the polymer electrolyte renders the conjugated compound and the polymer electrolyte sufficiently partially miscible in the solution such that the conjugated polymer and polymer electrolyte form the bicontinuous interpenetrating network having a nanometer scale phase size.

In this embodiment, a side chain of the conjugated compound that is not chemically compatible with the polymer electrolyte may form an interpenetrating network, in which the conjugated compound phase size is not in the order of nanometers. Adding a additive, however, that includes a surfactant having a polar end and a non-polar end builds an interconnecting bridge between the conjugated
compound and the polymer electrolyte such that the polar end of the bridge connects
to the polymer electrolyte and the non-polar end of the bridge connects to the
conjugated compound. As a result, more surface area of the conjugated compound is
exposed to the polymer electrolyte and a higher degree of interpenetration between the
conjugated compound and the polymer electrolyte is realized. Consequently, the
resulting conjugated compound phase size in the interpenetrating network is reduced
to a desired nanometer scale. Thus, in this embodiment, the appropriately selected
moieties, e.g., polar and non-polar moieties, of a surfactant, for example, admixed
with conjugated compound and polymer electrolyte blend facilitates in forming a
compact nanometer scale phase size of the present invention.

As mentioned above, addition of a judiciously chosen additive (e.g.,
surfactant) has the effect of optimizing the phase behavior of the bicontinuous
interpenetrating network and maximizing the interfacial area between the two phases.
The additive preferably has a relatively high dielectric constant to enhance the ionic
conductivity. Furthermore, the presence of additive improves electrochemical doping,
which in turn increases the density of electrochemically generated electrons and holes.
The additive also preferably has a relatively high boiling point and plasticizing
properties.

Representative surfactants employed in the present invention include N,N-
diethyldecanamide, stearamide, N-dodecylpyrrolidinone, octylcyanoacetate,
dodecanolactone and 2-tert-butylcyclohexanone and mixtures thereof.

If the chosen additive as mentioned above does not have the appropriate
plasticizing properties, a plasticizer may be added to the mixture of conjugated
compound, polymer electrolyte and additive. Those skilled in the art will recognize
that it is, however, preferable to employ an additive that facilitates in rendering the
conjugated compound miscible in the polymer electrolyte and also serves as a
plasticizer. The plasticizer employed in the present invention may include at least one
segment selected from the group consisting of ethylene oxide, polyethylene glycol,
propylene oxide, oxymethylene, epichlorohydran, bis-(methoxyethoxyethoxy)
phosphazene, oxetane, tetrahydrofuran, 1,3-dioxolane, ethylene imine, ethylene
succinate, ethylene sulfide, propylene sulfide, (oxyethylene) methacrylate,
(oxyethylene) oxymethylene, (oxyethylene) cyclotrisphosphazene, (2-(4-
carboxyhexafluorobutanoxyloxy) ethylmethacrylate), (2-sulfonethyl methacrylates),
methylene, ethylene, propylene, alkylene, acrylate, carbonate, styrene, ester, erethane,
siloxane, phosphazene, amide, imide, itaconate, glutamate, p-phenylterephthalate,
tetramethyl ammonium, tetraethyl ammonium, tetrapropyl ammonium, tetrabutyl
ammonium, tetradecyl ammonium, tribenzyl-phenyl ammonium, tetraphenyl ammonium, perchlorate, bromate, nitrate, sulfate, phosphate, tetrafluoroborate, hexafluorophosphate, aluminum tetrachlorate, n-butyrate, trifluoromethane sulfonate, trifluoromethane sulfonamide, acetate, trifluoroacetate, tetraphenylborate, toluene sulfonate, dodecylbenzene sulfonate, camphor sulfonate, picrate, salicylate, thiocyanate, benzoate, crown ethers, dimethylphthalate, dibutylphthalate, 1,2,4-butanetriol-trinitrate, pentabromo-diphenyl ether and arylphosphate, glycerine, sulfone amide, phosphate ester, benzoate ester and their derivatives.

Certain preferred processes of the present invention include forming the bicontinuous interpenetrating network of Figure 1 as follows: (i) preparing in a solvent, a solution of the polymer electrolyte and the conjugated compound; (ii) intimately mixing the solution; (iii) casting the solution in a substrate; and (iv) removing the solvent. Those skilled in the art will recognize that in the embodiment where a surfactant is required to form the interpenetrating network of the present invention, the surfactant may be mixed with the polymer electrolyte and conjugated compound before intimate mixing commences.

A process, according to one embodiment of the present invention, of forming electrochemical energy storage device 6 of Figure 1 begins when a conductive foil, e.g., a nickel foil, which serves as a current collector layer is deep cast in a dilute solution of conductive polymer to produce a film having a thickness of between about 0.02 micrometer and about 0.2 micrometer. Next, the conductive foil is deep cast in a highly viscous solution that includes a conjugated compound, a polymer electrolyte, salt, solvent (and additives if necessary as mentioned above). The conductive foil including the film of viscous solution is then dried to remove the solvent. The film produced may include a bicontinuous interpenetrating network having a nanometer scale phase size, as shown in Figure 2. A surfactant, octylcyanoacetate (OCA), may be added to the above-described mixture in a ratio (to the conjugated compound) of about 0.25:1 by weight. The resulting thickness of the electrode may be as high as about 1000 micrometer.

It is important to note that the solvent employed in the viscous solution may be a mixture of solvents and the solvents in the mixture preferably have similar solvation properties towards different soluble polymers, i.e. the polymer electrolyte and conjugated polymer. Furthermore, if the conjugated compound is dissolved in a first solvent and the polymer electrolyte is dissolved in a second solvent, then it is preferable to have the first and second solvents miscible in each other. In order to avoid precipitation when one of the two solvents in the mixture is being evaporated
and to ensure similar evaporation rates for the two solvents, the first and second solvents preferably have similar boiling points.

Before, during, or after the electrode is fabricated as described above, the separator may be fabricated. In one process, separator fabrication comprises a sequences of operations including (i)polymer solution preparation, (ii) casting of solution on substrate to form a thin film, (iii) evaporation of solvent, and (iv) lamination. The resulting film retains a fraction of the solvent (at a concentration of 5 to 75 weight %) as a plasticizer. Therefore, the major ingredients in the separator layer are: gelling polymer, plasticizer, and salt. Cross-linking can be used after film formation to enhance the film’s mechanical properties.

One specific method includes the following sequence.

1) Prepare a polymer solution containing a gelling polymer, one or more solvents, and one or more salts. These components may be selected from those listed above for example.

2) Cast (spread) the polymer solution on a substrate, preferably a non-sticking substrate, such as Teflon™. The thickness of the film may be controlled by using the doctor blade technique, for example.

3) Evaporate the excess solvent, using assistance of vacuum or heating or both if desired. After elimination of excess solvent, the solvent concentration in the film may range from 5 to 75 %, as desired.

4) Peel the separator film from non-sticking substrate and place it on a first electrode. The “placement” may take the form of lamination.

5) Place a second electrode on top of separator film. The entire structure may be laminated in one step assuming that there was no lamination after the operation #4. Alternatively two separate laminations may be performed: one for after each electrode has been placed on separator.

This method provides a relatively simple way to make a separator film. Nevertheless, care should be taken to ensure that the film does not tear during its separation from the substrate if the film is prepared to be very thin (e.g., less than 30 micrometers in thickness).

A related method employs the same sequence, except that the solution is cast directly on the first electrode. This allows very thin films to be made. It may have
the complication that the solvent may in certain cases dissolve the first electrode. This may be avoided by a judicious choice of solvent(s) for the separator solution that does not dissolve the first electrode. Dissolution of the first electrode by the solvent of the separator can also be prevented by cross-linking the surface of the first electrode before casting the separator solution.

In another method, a heated separator layer is spread on the electrode and cooled down to a gel form. While the gel solution is cooling down, a portion of gel layer may be cut off using a "doctor blade" technique to produce a thin gel film having a thickness of about 10 micrometers. The second electrode/current collector may then be mounted gently on top of the gel film to form the electrochemical energy storage device shown in Figure 1.

In a preferred embodiment of the present invention, a polymeric network by cross-linking is formed in the gel film and electrode layer before the electrode layers are assembled. Cross-linking enhances the film or layer's mechanical properties and raises the glass transition temperature. Conventional methods well known to those skilled in the art may be employed for fabricating ioni conductive networks, aqueous electrolytes that are cross-linked by radiation, acryloyl compounds that are cross-linked by polymerization, and a gel electrolyte as a "glue" to hold two electrodes together. Those skilled in the art will recognize that cross-linking applied to the polymer component in the separator layer and to the polymer components in the interpenetrating network of Figure 2 optimizes the film's mechanical, chemical, and thermodynamic stability.

In the above-described process, instead of a current collector layer, a dispersed carbon (at or above the percolation threshold) is introduced in the electrode film to increase the electrical conductivity within the electrode. A thick electrode layer is then prepared on a non-adhesive substrate (e.g., Teflon®).

The separator gel film employed in this embodiment may be dissolved in an ethylene carbonate and propylene carbonate solvent mixture, polyacrylonitrile and a salt in a ratio of 0.7:0.2:0.1 by weight. In an alternative embodiment, the cross-linked gel film is prepared by spreading a solution of monomer mixture and additives (e.g., cross-linking reagent) in an appropriate solvent or solvent mixture on a non-adhesive substrate (e.g., Teflon®). By way of example, the solution for preparing a cross-linked gel film includes poly(ethylene glycol), ethylene carbonate and propylene carbonate solvent mixture, a salt and a cross-linking reagent, such as dianhydride or a plasticizer mentioned above. While the solution is undergoing cooling, the gel film is cut off by the "doctor blade" technique to produce the film having a thickness of about 10
micrometers. The cross-linking of the gel film is then carried out (under heat and/or light, for example) to have a thin, cross-linked gel film. On top of the gel film, a high viscous solution of the electrode components is then applied and dried as mentioned above. Next, the two films are mounted on the current collector foil and the non-adhesive substrate is peeled off. The second electrode solution is then spread on the back side of the separator gel layer, dried and a second current collector is mounted on top of the second electrode layer to form a electrochemical energy storage device of the present invention.

In one example, a solution including a PPP derivative, e.g., poly[3’-(methyleneoxide-1,2-ethylenemethyloxide)-(1,4)-(1’,4’)-(1”’,4”’)-terphenylene], ionically conductive poly bis-(methoxyethoxyethoxy) phosphazene (MEEP), LiBF₄ (salt) was prepared in a chloroform solution in a ratio of about 1:0.3:0.45 by weight. The solution was then cast on a substrate according to conventional techniques well known to those skilled in the art and dried on the substrate at a temperature that is between about 0 and about 30 °C to produce a bicontinuous interpenetrating network having a phase size of nanometer scale.

In another example, a PPV precursor, e.g., poly(xylidenetetrahydrothiophenium chloride) was mixed with poly bis-(methoxyethoxyethoxy) phosphazene (MEEP) in a solvent mixture in a ratio of about 1:0.3:0.45 by weight. The solvent mixture included water and acetonitrile in a ratio of about 1:5 by volume. The solution was then cast on a substrate according to conventional techniques well known to those skilled in the art and dried on the substrate at a temperature of about 200 °C to produce a bicontinuous interpenetrating network having a phase size of nanometer scale. During the heating step, it was observed that the PPV precursor was transformed to PPV. This example illustrates that in one embodiment, a conjugated back-bone, without the assistance of a chemically compatible side-chain or surfactant and the like, by combining with an ionically conductive polymer electrolyte forms the bicontinuous interpenetrating network of nanometer scale phase size of the present invention.

After forming the bicontinuous interpenetrating network of the nanometer scale phase size, a differential thermal analysis (DTA) may be performed to show that the conjugated compound and polymer electrolyte are continuously and intimately mixed with each other. The thermal analysis will show an increased melting point for the polymer electrolyte, as compared to the normal melting point, when the conjugated compound and the polymer electrolyte are interpenetrating according to the present invention.
As mentioned before, secondary battery chemistries like Li-polymer require high quality, highly porous electrodes that are expensive. The present invention, however, fully exploits the conjugated polymer-based systems, which are inexpensive because of low cost polymer materials and polymer processing, and therefore effectively provides low-cost conjugated polymer-based electrochemical energy storage devices with energy densities comparable to commercially available secondary battery chemistries. Furthermore, as explained above, the electrochemical energy storage device of the present invention lends itself to thin film processability, which provides significant flexibility in the possible variety of device shapes and sizes. Judiciously chosen conjugated compounds and polymer electrolyte, for example, allow the present invention to provide a secondary battery with a capability to repeatedly discharge through an external load and recharge by an external energy source.

Although the foregoing invention has been described in some detail for purposes of clarity of understanding, it will be apparent that certain changes and modifications may be practiced within the scope of the appended claims. For example, while the specification has been described in terms of an electrochemical battery, there is in principal no reason why other electrochemical energy storage devices like a electrochemical energy capacitor cannot be fabricated by the teachings of the present invention. Therefore, the present embodiments are to be considered as illustrative and not restrictive, and the invention is not to be limited to the details given herein, but may be modified within the scope of the appended claims.
CLAIMS

What is claimed is:

1. A method of forming a polymer electrode for an electrochemical energy storage device, the method comprising:
   combining a conjugated compound and an ioniocally conductive polymer to form an electrode mixture; and
   forming the polymer electrode of predefined dimensions from the electrode mixture,
   wherein the polymer electrode has a bicontinuous interpenetrating network, in which the conjugated compound and the ioniocally conductive polymer form distinct continuous phases and wherein at least one continuous phase in the bicontinuous interpenetrating network has an average phase size of less than about 1 micrometer.

2. The method of claim 1, wherein the conjugated compound has an average phase size of less than about 1 micrometer.

3. The method of claim 1, wherein combining the conjugated compound and the ioniocally conductive polymer comprises preparing in a common solvent or solvent mixture a solution of the conjugated compound and the ioniocally conductive polymer.

4. The process of claim 3, wherein the solution further includes an additive that includes at least one of a surfactant and a plasticizer.

5. The process of claim 3, wherein the solvent or solvent mixture includes at least one material selected from the group consisting of propylene carbonate, ethylene carbonate, diethyl carbonate, dimethylcarbonate, dipropylcarbonate, dimethylsulfoxide, acetonitrile, dimethoxyethane, tetrahydrofuran, n-methyl-2-pyrrolidinone, chlorobenzene, N,N-dimethyl formamide, chloroform, ortho-dichlorobenzene (ODCB), γ-butyrolactone, poly(ethylene glycol), dibutyl phthalate, dioctyl phthalate and derivatives of the group of the materials.

6. The method of claim 3, further comprising:
   casting the solution on a substrate; and
   removing the solvent or solvent mixture to form the polymer electrode on the substrate.
7. The method of claim 6, wherein the casting includes casting on a current collector the solution of the ionically conductive polymer and the conjugated compound such that the current collector serves as the substrate.

8. The method of claim 7, further comprising dipping the current collector in a solution of the conjugated compound before the casting.

9. The method of claim 3, wherein the solution includes a surfactant having a first moiety that has an affinity for the conjugated compound and a second moiety that has an affinity for the ionically conductive polymer such that the presence of the surfactant in the solution makes the conjugated compound and the ionically conductive polymer at least partially miscible.

10. The method of claim 9, wherein the surfactant in the solution includes at least one compound selected from the group consisting of N,N-diethylidodecanamide, stearamide, N-dodecylpyrrolidinone, octylecyanacetate, dodecanolactone and 2-tert-butylcyclohexanone.

11. The method of claim 1, further comprising dispersing carbon particles in the polymer electrode in a concentration that is at least equal to the percolation threshold concentration, whereby at least one electrically conductive pathway forms from one end to another end of the polymer electrode.

12. The method of claim 1, wherein the conjugated compound includes a conjugated back-bone that is at least one of a substituted or an unsubstituted homopolymer, copolymer or oligomer having mer units selected from the group consisting of phenylene vinylene, phenylene, fluorene, quinoline, quinoxaline, acetylene, aniline, phenylene-2,6-benzobisthiazole, phenylene-2,6-benzobisoxazole, phenylene-2,6-benzimidazole, arylene, and arylene vinylene, and wherein the arylene is one of the following groups: naphthalene, anthracene, furylene, thiénylene, pyrrole, oxadiazole, selenylene and isothianaphthene.

13. The method of claim 12, wherein the conjugated compound further comprises a side-chain including at least one segment containing mer units selected from the group consisting of alkylene, acrylate, carbonate, styrene, ester, urethane, siloxane, phosphazene, amide, imide, nitrile, itaconate, glutamate, p-phenylterephthalate, ethylene oxide, propylene oxide, oxymethylene, epichlorohydran, bis-(methoxymethoxyethoxy) phosphazene, oxetane, tetrahydrofuran, 1,3-dioxolane,
ethylene imine, ethylene succinate, ethylene sulfide, propylene sulfide, (oxyethylene) methacrylate, (oxyethylene) oxymethylene and derivatives of the mer units of the group.

14. The method of claim 1, wherein the conjugated compound includes a non-conjugated back-bone and conjugated side chains,

wherein the non-conjugated back-bone includes mer units selected from the group consisting of alkylene, acrylate, carbonate, styrene, ester, urethane, siloxane, phosphazene, amide, imide, nitrile, itaconate, glutamate, p-phenylterephthalate, ethylene oxide, propylene oxide, oxymethylene, epichlorohydran, bis-(methoxyethoxyethoxy) phosphazene, oxetane, tetrahydrofuran, 1,3-dioxolane, ethylene imine, ethylene succinate, ethylene sulfide, propylene sulfide, (oxyethylene) methacrylate, (oxyethylene) oxymethylene, (oxyethylene) cyclotrisphosphazene, (2-(4-carboxyhexafluorobutanoxyloxy) ethylmethacrylate) and derivatives of the compounds of the group and

wherein the conjugated side-chains include a substituted or an unsubstituted homopolymer, copolymer or oligomer having mer units selected from the group consisting of phenylene vinylene, phenylene, fluorene, quinoline, quinoxaline, acetylene, aniline, phenylene-2,6-benzobistiazole, phenylene-2,6-benzobisoxazole, phenylene-2,6-benzimidazole, arylene, and arylene vinylene, wherein arylene is one compound selected from the group consisting of naphthalene, anthracene, furylene, thiénylene, pyrrole, oxadiazole, selenylene or isothianaphthene.

15. The method of claim 1, wherein the ionically conductive polymer includes mer units selected from a group consisting of ethylene oxide, propylene oxide, oxymethylene, epichlorohydran, bis-(methoxyethoxyethoxy) phosphazene, oxetane, tetrahydrofuran, 1,3-dioxolane, ethylene imine, nitrile, ethylene succinate, ethylene sulfide, propylene sulfide, (oxyethylene) methacrylate, (oxyethylene) oxymethylene, (oxyethylene) cyclotrisphosphazene, (2-(4-carboxyhexafluorobutanoxyloxy) ethylmethacrylate) and derivatives of the mer units of the group.

16. The method of claim 1, wherein the ionically conductive polymer includes a polyelectrolyte and a counter ion, wherein the polyelectrolyte includes a polymer or polymer component selected from the group consisting of (2-sulfonemethyl methacrylates), (diallyldimethyl ammonium) chloride, (styrene sulfonate), nafion 117, (p-phenylene terephthalamide sulfonate) salts, oligo (ethylene oxide) methacrylate-co-methacrylate salt and derivatives of the polymer or the copolymer of the group.
17. The method of claim 1, further comprising forming the polymer electrode with a salt containing one or more cations selected from the group consisting of lithium, sodium, potassium, rubidium, cesium, aluminum, cobalt, silver, barium, calcium, copper, zinc, manganese, magnesium, chromium, ammonium, tetramethyl ammonium, tetraethyl ammonium, tetrabutyl ammonium, tribenzyl-phenyl ammonium and tetrphenyl ammonium, the salt also containing one or more anions selected from the group consisting of fluoride, chloride, bromide, iodide, perchlorate, bromate, nitrate, sulfate, phosphate, tetrafluoroborate, hexafluorophosphate, aluminum tetrachlorate, n-butyrate, trifluoromethane sulfonate, trifluoromethane sulfonamide, acetate, trifluoracetate, tetraphenylborate, toluene sulfonate, dodecylbenzene sulfonate, camphor sulfonate, picrate, salicylate, thiocyanate and benzoate.

18. The method of claim 1, wherein the average diameter of a strand of the conjugated compound is between about 1 nanometer and about 1 micrometer.

19. The method of claim 1, wherein the conjugated compound has an energy gap that is at least about 1 eV.

20. The method of claim 1, wherein the conjugated compound has a side chain that has an affinity for the ionically conductive polymer such that the conjugated compound and the ionically conductive polymer are at least partially miscible.

21. The method of claim 1, wherein ionically conductive polymer has a side chain that has an affinity for the conjugated compound such that the conjugated compound and the ionically conductive polymer are at least partially miscible.

22. A method of preparing an electrochemical energy storage device from a polymer electrode prepared as recited in claim 1, the method comprising:

   providing a separator layer that is electronically non-conductive; and

   assembling the separator layer, the polymer electrode, and a counter electrode such that the separator facilitates the transport of ions to and from the polymer electrode.

23. The process of claim 22, wherein forming the separator layer includes (i) casting a solution of gelling polymer, solvent, and salt to form film; and (ii) evaporating at least a portion of the solvent.
24. The process of claim 23, further comprising cross-linking the gelling polymer.

25. The process of claim 22, wherein the separator layer is a blend of polymers and the blend of polymers include at least one material selected from the group consisting of polyethylene, polypropylene, polytetrafluoroethylene, polystyrene, polyethylene terephthalate and nylon.

26. A polymer electrode for an electrochemical energy storage device, the polymer electrode comprising:
   a conjugated compound; and
   an ionically conductive polymer,
   wherein the polymer electrode has a bicontinuous interpenetrating network, in which the conjugated compound and the ionically conductive polymer form distinct continuous phases and wherein at least one continuous phase in the bicontinuous interpenetrating network has an average phase size of less than about 1 micrometer.

27. The polymer electrode of claim 26, wherein carbon particles are dispersed in the polymer electrode and a concentration of the dispersed carbon particles is greater than or about equal to a percolation threshold concentration, whereby at least one electrically conductive pathway exists from one end to another end of the polymer electrode.

28. The polymer electrode of claim 26, wherein the conjugated compound includes a conjugated back-bone that is at least one of a substituted or an unsubstituted homopolymer, copolymer or oligomer having mer units selected from the group consisting of phenylene vinylene, phenylene, fluorene, quinoline, quinoxaline, acetylene, aniline, phenylene-2,6-benzobisthiazole, phenylene-2,6-benzobisoxazole, phenylene-2,6-benzimidazole, arylene, and arylene vinylene, and wherein the arylene is one of the following groups: naphthalene, anthracene, furylene, thiénylene, pyrrole, oxadiazole, selenylene and isothianaphthene.

29. The polymer electrode of claim 28, wherein the conjugated compound further comprises side-chains including at least one segment containing mer units selected from the group consisting of alkylene, acrylate, carbonate, styrene, ester, urethane, siloxane, phosphazene, amide, imide, nitrile, itaconate, glutamate, p-phenylterephthalate, ethylene oxide, propylene oxide, oxymethylene, epichlorohydrin, bis-(methoxyethoxyethoxy) phosphazene, oxetane, tetrahydrofuran,
1,3-dioxolane, ethylene imine, ethylene succinate, ethylene sulfide, propylene sulfide, (oxyethylene) methacrylate, (oxyethylene) oxymethylene and derivatives of the mer units of the group.

30. The polymer electrode of claim 26, wherein conjugation in the electronic conductive conjugated compound extends for greater than or equal to 3 basic conjugation units.

31. The polymer electrode of claim 26, wherein the conjugated compound includes a non-conjugated back-bone and conjugated side chains,

wherein the non-conjugated back-bone includes mer units selected from the group consisting of alkylene, acrylate, carbonate, styrene, ester, urethane, siloxane, phosphazene, amide, imide, nitrile, itaconate, glutamate, p-phenylterephthalate, ethylene oxide, propylene oxide, oxymethylene, epichlorohydran, bis-(methoxyethoxyethoxy) phosphazene, oxetane, tetrahydrofuran, 1,3-dioxolane, ethylene imine, ethylene succinate, ethylene sulfide, propylene sulfide, (oxyethylene) methacrylate, (oxyethylene) oxymethylene, (oxyethylene) cyclotrissphosphazene, (2-(4-carboxyhexafluorobutanoxyloxy) ethylmethacrylate) and derivatives of the compounds of the group and

wherein the conjugated side-chains include a substituted or an unsubstituted homopolymer, copolymer or oligomer having mer units selected from the group consisting of phenylene vinylene, phenylene, fluorene, quinoline, quinoxaline, acetylene, aniline, phenylene-2,6-benzobistiazole, phenylene-2,6-benzobisoxazole, phenylene-2,6-benzimidazole, arylene, and arylene vinylene, wherein arylene is one compound selected from the group consisting of naphthalene, anthracene, furylene, thiophene, pyrrole, oxadiazole, selenylene or isotrianaphthene.

32. The polymer electrode of claim 26, wherein the ionically conductive polymer has an ionic conductivity that is at least about 100 times greater than an electronic conductivity of the ionically conductive polymer.

33. The polymer electrode of claim 26, wherein the ionically conductive polymer is complexed with a salt.

34. The polymer electrode of claim 26, wherein the ionically conductive polymer includes mer units selected from a group consisting of ethylene oxide, propylene oxide, oxymethylene, epichlorohydran, bis-(methoxyethoxyethoxy) phosphazene, oxetane, tetrahydrofuran, 1,3-dioxolane, ethylene imine, nitrile, ethylene succinate,
ethylene sulfide, propylene sulfide, (oxyethylene) methacrylate, (oxyethylene) oxymethylene, (oxyethylene) cyclotrisphosphazene, (2-(4-carboxyhexafluorobutanoxyloxy) ethylmethacrylate) and derivatives of the mer units of the group.

35. The polymer electrode of claim 26, wherein the ionically conductive polymer includes a polyelectrolyte and a counter ion, wherein the polyelectrolyte includes a polymer or polymer component selected from the group consisting of (2-sulfonethyl methacrylates), (diallyldimethyl ammonium) chloride, (styrene sulfonate), nafion 117, (p-phenylene terephthalamide sulfonate) salts, oligo (ethylene oxide) methacrylate-co-methacrylate salt and derivatives of the polymer or the copolymer of the group.

36. The polymer electrode of claim 26, further comprising a salt having at least one cation selected from the group consisting of lithium, sodium, potassium, rubidium, cesium, aluminum, cobalt, silver, barium, calcium, copper, zinc, manganese, magnesium, chromium, ammonium, tetramethyl ammonium, tetraethyl ammonium, tetrapropyl ammonium, tetrabutyl ammonium, tetradecyl ammonium, tribenzyl-phenyl ammonium and tetraphenyl ammonium, and having at least one anion selected from the group consisting of fluorine, chlorine, bromine, iodine, perchlorate, bromate, nitrate, sulfate, phosphate, tetrafluoroborate, hexafluorophosphate, aluminum tetrachlorate, n-butylate, trifluoromethane sulfonate, trifluoromethane sulfonamide, acetate, trifluoracetate, tetraphenylborate, toluene sulfonate, dodecylbenzene sulfonate, camphor sulfonate, picrate, salicylate, thiocyanate and benzoate.

37. The polymer electrode of claim 26, wherein the average diameter of a strand of the conjugated compound is between about 1 nanometer and about 1 micrometer.

38. The polymer electrode of claim 26, wherein the conjugated compound has an energy gap that is at least about 1 eV.

39. The polymer electrode of claim 38, wherein the conjugated compound has an energy gap that is more than about 2 eV.

40. The polymer electrode of claim 26, further comprising a plasticizer selected from the group consisting of ethylene oxide, polyethylene glycol, propylene oxide, oxymethylene, epichlorohydran, bis-(methoxyethoxyethoxy) phosphazene, oxetane, tetrahydrofuran, 1,3-dioxolane, ethylene imine, ethylene succinate, ethylene sulfide,
propylene sulfide, (oxyethylene) methacrylate, (oxyethylene) oxymethylene, (oxyethylene) cyclotrisphosphazene, (2-(4-carboxyhexafluorobutanoxyloxy) ethylmethacrylate), (2-sulfonethyl methacrylates), methylene, ethylene, propylene, alkylene, acrylate, carbonate, styrene, ester, ethane, siloxane, phosphazene, amide, imide, itaconate, glutamate, p-phenylterephthalate, tetramethyl ammonium, tetraethyl ammonium, tetrapropyl ammonium, tetrabutyl ammonium, tetradecyl ammonium, tribenzyl-phenyl ammonium, tetraphenyl ammonium, perchlorate, bromate, nitrate, sulfate, phosphate, tetrafluoroborate, hexafluorophosphate, aluminum tetrachlorate, n-butyrate, trifluoromethane sulfonate, trifluoromethane sulfonamide, acetate, trifluoroacetate, tetraphenylborate, toluene sulfonate, dodecylbenzene sulfonate, camphor sulfonate, picrate, salicylate, thiocyanate, benzoate, crown ethers, dimethylphthalate, dibutylphthalate, 1,2,4-butrantriol-trinitrate, pentabromo-diphenyl ether, arylphosphate, glycerine, sulfone amide, phosphate ester, benzoate ester and derivatives thereof.

41. The polymer electrode of claim 26, further comprising a surfactant having a first moiety that has an affinity for the conjugated compound and a second moiety that has an affinity for the ionically conductive polymer such that the presence of the surfactant in the solution makes the conjugated compound and the ionically conductive polymer at least partially miscible.

42. The polymer electrode of claim 41, wherein the surfactant includes at least one compound selected from the group consisting of N,N-diethyldecanamide, stearamide, N-dodecylpyrrolidinone, octylcyanoacetate, dodecanolactone and 2-tert-butylcyclohexanone.

43. The polymer electrode of claim 26, wherein the conjugated compound has a side chain that has an affinity for the ionically conductive polymer such that the conjugated compound and the ionically conductive polymer are at least partially miscible.

44. The polymer electrode of claim 26, wherein ionically conductive polymer has side chains that have an affinity for the conjugated compound such that the conjugated compound and the ionically conductive polymer are at least partially miscible.

45. The polymer electrode of claim 44, wherein the side-chains include at least one segment having mer units selected from the group consisting of methylene, ethylene, propylene, alkylene, acrylate, carbonate, styrene, ester, urethane, siloxane,
phosphazene, amide, imide, nitrile, itaconate, glutamate, p-phenylterephthalate, ethylene oxide, propylene oxide, oxymethylene, epichlorohydran, bis-(methoxyethoxyethoxy) phosphazene, oxetane, tetrahydrofuran, 1,3-dioxolane, ethylene imine, ethylene succinate, ethylene sulfate, propylene sulfide, (oxyethylene) methacrylate, (oxyethylene) oxymethylene and derivatives of the mer units of the group.

46. An electrochemical energy storage device comprising:

a polymer electrode as recited in claim 26;

a counterelectrode; and

a separator that is electronically non-conductive and contacts the polymer electrode in a manner allowing the transport of ions to and from the polymer electrode.

47. The electrochemical energy storage device of claim 46, further comprising a current collector that is in electrical contact with the polymer electrode.

48. The electrochemical energy storage device of claim 46, wherein the separator is a gel electrolyte that conducts ions to and from the polymer electrode and includes at least one of a polymer, copolymer and oligomer having mer units selected from the group consisting of substituted or unsubstituted vinylidene fluoride, urethane, ethylene oxide, propylene oxide, acrylonitrile, methy lactacrylate, alkylacrylate, acrylamide, vinyl acetate, vinylpyrrolidinone, tetraethylene glycol diacrylate, phosphazene and dimethylsiloxane.

49. The electrochemical energy storage device of claim 46, wherein the counterelectrode includes a polymer electrode as recited in claim 26.

50. The electrochemical energy storage device of claim 46, wherein the counterelectrode includes at least one material selected from the group consisting of alkali metals, alkali metal alloys, and alkali metal insertion compounds.

51. The electrochemical energy storage device of claim 46, wherein the electrochemical energy storage device is a secondary battery.
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- column 3, line 51 -column 4, line 17
- column 5, line 11 - line 29
- column 5, line 49 -column 6, line 4
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example 1

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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Data of mailing of the international search report: 27/10/1999

Name and mailing address of the ISA:
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk
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Authorized officer:
Gamez, A
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- column 8, line 45 - column 9, line 8
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