In a second embodiment, an ultracapacitor is provided that includes:

(a) first and second carbon-based electrodes; and

(b) a solid-phase electrolyte material comprising an ionic liquid and a polymer host, the polymer host forming a self-supporting film comprising the ionic liquid.

Preferably, the ionic liquid includes one or more cations selected from the group consisting essentially of pyridinium, pyridazinium, pyrimidinium, pyrazinium, imidazolium, pyrazolium, thiazolium, oxazolium, triazolium, ammonium, pyrrolidinium, pyrrolinium, pyrrolium, piperidinium, phosphonium, and mixtures thereof and one or more anions selected from the group consisting essentially of F^-; Cl^-, Br^-; I^-; NO_3^-; $N(CN)_2^-$; BF_4^-; ClO_4^-; PF_6^-; RSO_3^-; $RCOO^-$; where R is an alkyl group, substituted alkyl group, or phenyl group; $(CF_3)_2PF_4^-$, $(CF_3)_3PF_3^-$, $(CF_3)_4PF_2^-$, $(CF_3)_5PF^-$, $(CF_3)_6P^-$, $(CF_2SO_3^-)_2$, $(CF_2CF_2SO_3^-)_2$, $(CF_3SO_2^-)_2N^-$, $CF_3CF_2(CF_3)_2CO^-$, $(CF_3SO_2^-)_2CH^-$, $(SF_5)_3C^-$, $(CF_3SO_2)_3C^-$, $[O(CF_3)_2C_2(CF_3)_2O]_2PO^-$, $(CF_3(CF_2)_7SO_3^-$, and mixtures thereof.

Preferably, the polymer host is selected from the group consisting essentially of homopolymers and copolymers of polyolefins, polystyrenes, polyvinyls, polyacrylics, polyhalo-olefins, polydienes, polyoxides/esthers/acetals, polysulfides, polyesters/thioesters, polyamides/thioamides, polyurethanes/thiourethanes, polyureas/thioureas, polyimides/thioimides, polyanhydrides/thianhydrides, polycarbonates/thiocarbonates, polyimines, polysiloxanes/silanes, polyphosphazenes, polyketones/thioketones, polysulfones/sulfoxides/sulfonates/sulfoamides, polyphylenes, and mixtures thereof.

The solid-phase electrolyte material can include a substantially nonconductive, inorganic filler having a surface area of at least about 10 m^2/g, a maximum dimension of about 50 micrometers, and an average pore size of less than about 10 micrometers.

In a third embodiment, a method is provided that includes the steps:

(a) contacting a polymer host with an organic solvent to form a first composition;

(b) contacting an ionic liquid with the first composition; and

(c) removing at least most of the organic solvent from the first composition to form a freestanding film comprising the polymer host and ionic liquid.

Figs 26A-B are cyclic voltammograms obtained in [EMIM][Tf_2N] for aligned CNT electrodes without (a) and with (b) plasma etching on the CNT film (the scan rate being 20 mV/s and capacitance being indicated in the CVs);

Fig. 27 is a table listing ionic liquid structures and characteristics;

Fig. 28 provides Ragone plots of AC/IL and CNT/IL capacitors (with the charge/discharge current density being 2 ~ 50 mA/cm^2);

Fig. 29 is a plot of capacitance (bottom) obtained in [EMIM][Tf_2N] for aligned CNT electrodes without and with plasma etching on one side and two sides of the CNT film;

Fig. 30 is a plot of capacitance versus scan rate showing the effect of scan rate on capacitance of aligned CNT electrodes obtained in different ionic liquids (data being from Figs. 28A-D);

Fig. 31 is a plot of Z'' against Z' providing AC impedance spectra obtained for aligned CNT electrodes in [EMIM][BF_4] (a), [EMIM][Tf_2N] (b), and [EMIM][CF_3SO_3] (c) and for an activated carbon electrode in [EMIM][Tf_2N] (d) (with AC voltage amplitude being 5mV, frequency range being 100K Hz-1 mHz, and the activated carbon electrode having a specific surface area of 1000~2000 m^2/g and a thickness of 150μm);

Figs. 32A-C are CVs of aligned CNT electrodes obtained in [EMIM][BF_4] (Fig. 32A), [EMIM][Tf_2N] (Fig. 32B), and [EMIM][CF_3SO_3] (Fig. 32C) (with scan rate increasing from 5, 20, 50, to 100 mV/s as indicated by arrows);

Figs. 33A-B provide CVs (Fig. 33A) and capacitance (Fig. 33B) obtained for an activated carbon electrode in [EMIM][Tf_2N] (with scan rate increasing from 5, 20, 50, to 100 mV/s as indicated by arrows);

Figs. 34A-B provide CVs of an ultracapacitor fabricated from activated carbon electrodes and [EMIM][Tf_2N], AC/IL capacitor (with Fig. 34A being from 0~3V and Fig. 34B being from 0~4V and the scan rate increasing from 5, 20, 50, 100, to 200 mV/s as indicated by arrows);

Figs. 35A-B are CVs of an ultracapacitor fabricated from aligned CNT electrodes and [EMIM][Tf_2N], CNT/IL capacitor (with Fig. 35A being from 0~3V and Fig. 35B being from 0~4V and the scan rate increasing from 5, 20, 50, 100, to 200 mV/s as indicated by arrows);

b. a C_5 to C_{30} cycloaliphatic hydrocarbon radical substituted with at least one of the following Cl, Br, F, I, NH, OH, NH_2, $NHCH_3$ or SH

c. a hydroxyl

d. an amine

e. a thiol

(o) a polyether of the type $-O-(-R_7-O-)_n-R_8$ or block or random type $-O-(-R_7-O-)_n-(-R_{7'}-O-)_m-R_8$ where

a. R_7 is a linear or branched hydrocarbon radical having from 2 to 4 carbon atoms

b. $R_{7'}$ is a linear or branched hydrocarbon radical having from 2 to 4 carbon atoms

c. n is from 1 to 40

d. R_8 is hydrogen, or a C_5 to C_{30} straight-chain or branched hydrocarbon radical, or a C_5 to C_{30} cycloaliphatic hydrocarbon radical, or a C_6 to C_{30} aromatic hydrocarbon radical, or a C_7 to C_{40} alkylaryl radical

(p) a polyether of the type $-O-(-R_7-O-)_n-C(O)-R_8$ or block or random type $-O-(-R_7-O-)_n-(-R_{7'}-O-)_m-C(O)-R_8$ where

a. R_7 is a linear or branched hydrocarbon radical having from 2 to 4 carbon atoms

b. $R_{7'}$ is a linear or branched hydrocarbon radical having from 2 to 4 carbon atoms

c. n is from 1 to 40

d. R_8 is hydrogen, or a C_5 to C_{30} straight-chain or branched hydrocarbon radical, or a C_5 to C_{30} cycloaliphatic hydrocarbon radical, or a C_6 to C_{30} aromatic hydrocarbon radical, or a C_7 to C_{40} alkylaryl radical.

The anionic component is preferably selected from the group consisting essentially of:

(a) halides, i.e., chloride, bromide, and iodide, preferably iodide

(b) phosphates

(c) halophosphates, preferably hexafluorophosphate

to the strongly electron-withdrawing functional group –C–F. PVdF co-polymerized with hexafluoropropylene (PVdF-HFP), can be used to improve the gel properties of the polymer electrolytes because of its greater solubility in organic solvents, lower crystallinity, and lower glass transition temperature than the PVdF polymer alone in the gel.

In a preferred polymer composition, the mass ratios of ionic liquid to polymer host range from about 0.1:1 to about 1:1 and even more preferably from about 0.1:1 to about 10:1. Stated another way, the ILGPE layer 116 preferably comprises from about 9 to about 50 and even more preferably from about 9 to about 90 wt.% ionic liquid, with the remainder being the polymer host.

The ionic liquid can include additives to provide more desirable electrochemical properties. By way of example, viscosity reducers can be added to the ionic liquid to lower viscosity and increase ionic conductivity for ILGPEs. Examples of potential viscosity reducers include propylene carbonate, ethylene carbonate, dimethylformamide, and acetonitrile.

In an alternative configuration, the layer 116 includes an inorganic filler in addition to the ionic liquid and polymer host. The filler increases the mechanical strength of the ILGPE layer 116 and decreases the level of crystallinity of the polymer host. Introduction of inorganic fillers disrupts polymer chain packing (and crystallinity) and thus enhances ionic conductivities for the ILPGE layer 116. The filler preferably has a high surface area (*e.g.,* preferably a surface area of at least about 10 and more preferably ranging from about 10 to about 500 m^2/g) and electrochemical inertness (*e.g.,* is insulative or nonconductive) to avoid shorting the opposing electrodes. Preferred fillers include zeolites, metal oxides such as ZrO_2, TiO_2, and Al_2O_3, hydrophobic fumed silica, fiberglass, silicates, cellulosic materials, lignin, diatomaceous earth, and mixtures thereof. At least most of the filler particles, and more preferably at least about 80% of the particles, have a particle size preferably not greater than about 50 microns. The particles have a preferred maximum dimension of about 50 micrometers, more preferably about 25 micrometer, even more preferably about 10 micrometers, and even more preferably about 5 micrometers and a preferred average pore size of less than about 10 micrometers and more preferably of no more than about 5 micrometers. The pores preferably constitute from about 25 to about 95 percent by volume of the microporous

Thermal properties of ILGPEs were screened by performing selected measurements using Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA). Different instruments were used with common samples in order to identify any instrumental artifacts—none were determined to exist. The DSC was performed using either a TA DSC Q1000 or a PE Pyris 1 DSC. These measurements were made using "crimped" Al pans. The DSC was run to a maximum of 200°C with a low temperature (using liquid N_2) of 0°C or (-100°C for a few samples). Sample size was typically ~ 25 mg and runs had one heating cycle from room temperature, then a cooling cycle to 0°C (or lower), and then a final heating cycle using a 10°C/min ramp with a 1 minute hold at the end points. The TGA was performed using either a Sieko TG/DTA200 or a TA TGA Q500. In either case, the purge gas was N_2, the sample size was ~ 7 - 10 mg (Pt pans), and the TGA was performed between 30 - 700 °C using a 60 minute hold at the starting (for baseline stabilization) and end points and a heating rate of 5°C/min.

With respect to the calorimetry (DSC) results, it was found that during the first heating cycle a small, broad endotherm occurred between 80-120°C. This would be consistent with the TGA results and could be water being evaporated or, alternatively, a low order structural re-arrangement. The cooling cycle generated a small, broad exotherm usually in the range of 40-70°C. The second heating cycle was generally consistent with the first one. No glass transition-type events were identified. The ILGPE's based on the imbibed Gore-Tex® membrane (PTFE) were different than the others in that a small transition (perhaps the crystallization of PTFE) was identified and the broad endotherm between 80-120°C wasn't discerned—probably due to less water and no NMP, and consistent with the lowest mass loss (0.4%) observed in the TGA measurements. In general, the heat capacity of the samples decreased continuously as the temperature increased between 80 – 200°C. In general, the DSC measurements indicate some variations in the thermal transitions depending on whether the matrix was PVdF-HFP, PVdF-HFP + zeolite, or PTFE. The presence of the zeolite resulted in bimodal transitions and long continuous changes in the heat capacity as the temperature increased.

Thermal stability of ILGPEs was measured by thermogravimetric analysis (TGA) (mass loss resulting from increasing temeperature) by measuring the weight loss of the gel with increasing temperature. Fig. 18 shows the TGA result of PVdF-

What is claimed is:

1. An ~~ultracapacitor~~electrochemical energy storage device, comprising:

(a) first and second electrodes, the first and second electrodes being oppositely charged ~~electrodes~~ and primarily comprising substantially aligned carbon nanotubes, the aligned carbon nanotubes having opposing first and second ends; and

(b) an electrolyte material, comprising oppositely charged ions, in contact with at least most of the first ends of the aligned carbon nanotubes of the first and second electrodes, wherein at least ~~most~~ one of the first ends ~~of~~ in contact with the ~~carbon nanotubes~~ electrolyte material is ~~are~~ open to permit the charged ions to access an interior surface~~s~~ of the ~~nanotubes~~corresponding carbon nanotube, wherein the ~~sizes of the~~ charged ions ~~are~~ have a size less than the corresponding carbon nanotube interior diameter~~s of~~, and wherein the carbon nanotubes have been etched and amorphous carbon covering the carbon nanotube surface has been removed.

2. The ~~ultracapacitor~~ electrochemical energy storage device of claim 1, wherein longitudinal axes of at least most of the aligned carbon nanotubes ~~are~~ of the first and second electrodes are substantially parallel to one another along substantially the entire length of the carbon nanotube and wherein at least most of the ~~carbon nanotubes are carbon nanotubes~~first ends in one or both of the first and second electrodes are open.

3. The ~~ultracapacitor~~ electrochemical energy storage device of claim 1, wherein at least most of the opposing second ends of the aligned carbon nanotubes in one or both of the first and second electrodes are open, and wherein the charged ions comprise at least one of pyridinium, pyridazinium, pyrimidinium, pyrazinium, imidazolium, pyrazolium, thiazolium, oxazolium, triazolium, ammonium, pyrrolidinium, pyrrolinium, pyrrolium, and piperidinium.

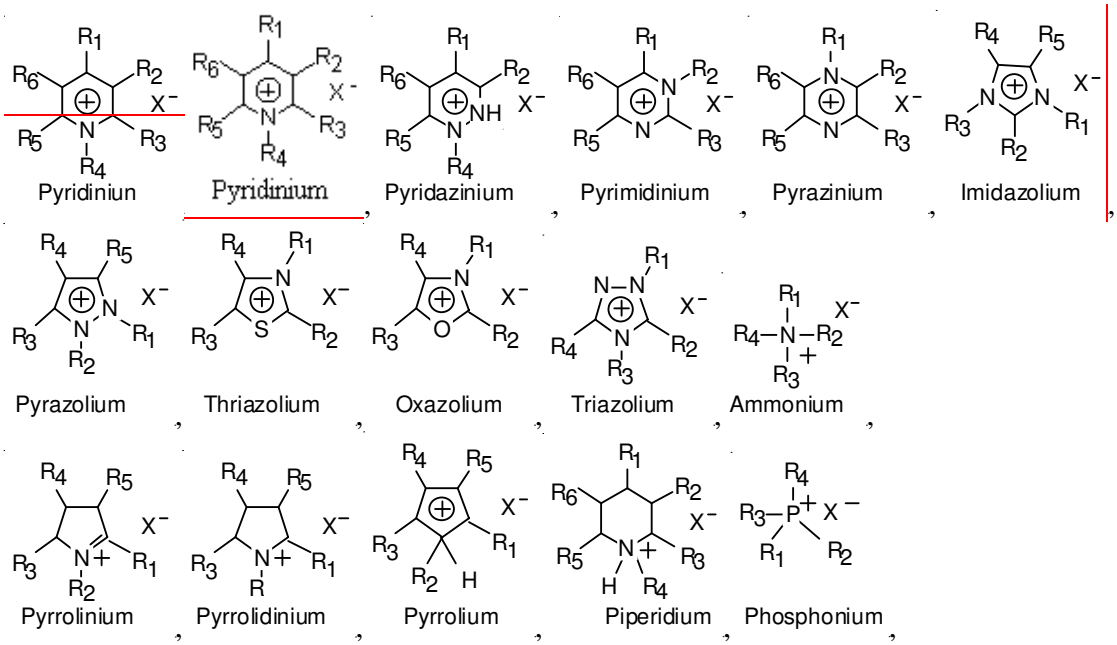
4. The ~~ultracapacitor~~ electrochemical energy storage device of claim 1, wherein at least most of the aligned carbon nanotubes comprising the first and second electrodes have lengths of at least about 75 microns, inter-carbon nanotube spacings ranging from about 5 to about 1,000 nm, and diameters ranging from about 0.25 to about 250 nm.

5. The ~~ultracapacitor~~ electrochemical energy storage device of claim 1, wherein the electrolyte material comprises an ionic liquid ~~and polymer host in the form of a self-supporting film, wherein the ionic liquid has~~having a melting point of no more than about 100 degrees Celsius, a decomposition temperature of at least about 200 degrees Celsius, a viscosity of no more than about 200 Cp, an ionic conductivity of at least about 0.1 mS/cm, and an electrochemical window of at least about 2 Volts.

6. The ~~ultracapacitor~~ electrochemical energy storage device of claim 5, wherein~~:~~

~~(I)~~ the ionic liquid comprises:

(A) at least one cation selected from the group of cations consisting ~~essentially~~ of the following compounds and mixtures thereof:



wherein R_1, R_2, R_3, R_4, R_5, and R_6 of the cationic components are identical or different and are selected from the group consisting ~~essentially~~ of:

(i) a hydrogen;

(ii) a halogen;

(iii) a hydroxyl;

(iv) an amine;

(v) a thiol;

(vi) a C_1 to C_{25} straight-chain~~,~~ or branched aliphatic hydrocarbon radical;

(vii) a C_5 to C_{30} cycloaliphatic hydrocarbon radical;

(viii) a C_6 to C_{30} aromatic hydrocarbon radical;

(ix) a C_7 to C_{40} alkylaryl radical;

(x) a C_2 to C_{25} linear or branched aliphatic hydrocarbon radical having interruption by one or more heteroatoms, such as, oxygen, nitrogen or sulfur;

(xi) a C_2 to C_{25} linear or branched aliphatic hydrocarbon radical having interruption by one or more functionalities selected from the group of hydrocarbon radials consisting ~~essentially~~ of:

(a') a carbonyl;

(b') an ester;

(c') an amide, where R' is selected from the group consisting ~~essentially~~ of hydrogen, C_1-C_{12} straight-chain, branched or cyclic alkane or alkene;

(d') a sulfonate;

(e') a sulfonamide, where R' is selected from the group consisting ~~essentially~~ of hydrogen, C_1-C_{12} straight-chain, branched or cyclic alkane or alkene;

(xii) a C_2 to C_{25} linear or branced aliphatic hydrocarbon radical terminally functionalized by Cl, Br, F, I, NH, OH, NH_2, $NHCH_3$ or SH;

(xiii) a C_5 to C_{30} cycloaliphatic hydrocarbon radical having at least one heteroatom selected from the group of heteroatoms consisting ~~essentially~~ of O, N, S, and optionally substituted with at least one of the following Cl, Br, F, I, NH, OH, NH_2, $NHCH_3$ or SH;

(xiv) a C_7 to C_{40} alkylaryl radical having at least one heteroatom selected from the group of heteroatoms consisting ~~essentially~~ of O, N, S, and optionally substituted with at least one of the following:

(a'') a C_2 to C_{25} straight-chain, or branched hydrocarbon radical substituted with at least one of the following Cl, Br, F, I, NH, OH, NH_2, $NHCH_3$ or SH;

(b'') a C_5 to C_{30} cycloaliphatic hydrocarbon radical substituted with at least one of the following Cl, Br, F, I, NH, OH, NH_2, $NHCH_3$ or SH

(c'') a hydroxyl;

(d'') an amine;

(e'') a thiol;

(xv) a polyether of the type $-O-(-R_7-O-)_n-R_8$ or block or random type $-O-(-R_7-O-)_n-(-R_{7'}-O-)_m-R_8$,wherein at least one of the following is true:

(a''') R_7 is a linear or branched hydrocarbon radical having from 2 to 4 carbon atoms;

(b''') $R_{7'}$ is a linear or branched hydrocarbon radical having from 2 to 4 carbon atoms; and

(c''') wherein n is from 1 to 40; and

(d''') R_8 is hydrogen, or a C_5 to C_{30} straight-chain or branched hydrocarbon radical, or a C_5 to C_{30} cycloaliphatic hydrocarbon radical, or a C_6 to C_{30} aromatic hydrocarbon radical, or a C_7 to C_{40} alkylaryl radical; and

(xvi) a polyether of the type $-O-(-R_7-O-)_n-C(O)-R_8$ or block or random type $-O-(-R_7-O-)_n-(-R_{7'}-O-)_m-C(O)-R_8$,wherein at least one of the following is true:

(a'''') R_7 is a linear or branched hydrocarbon radical having from 2 to 4 carbon atoms;

(b'''') $R_{7'}$ is a linear or branched hydrocarbon radical having from 2 to 4 carbon atoms; and

(c'''') wherein n is from 1 to 40; and

(d'''') R_8 is hydrogen, or a C_5 to C_{30} straight-chain or branched hydrocarbon radical, or a C_5 to C_{30} cycloaliphatic hydrocarbon radical, or a C_6 to C_{30} aromatic hydrocarbon radical, or a C_7 to C_{40} alkylaryl radical; and

(B) at least one anion selected from the group of anions consisting ~~essentially~~ of F^-; Cl^-, Br^-; I^-; NO_3^-; $N(CN)_2^-$; BF_4^-; ClO_4^-; PF_6^-; RSO_3^-; $RCOO^-$; where R is an alkyl group, substituted alkyl group, or phenyl group; $(CF_3)_2PF_4^-$~~,~~ ~~-~~; $(CF_3)_3PF_3^-$~~,~~ ~~-~~; $(CF_3)_4PF_2^-$~~,~~ ~~-~~; $(CF_3)_5PF^-$~~,~~ ~~-~~; $(CF_3)_6P^-$~~,~~ ~~-~~; $(CF_2SO_3^-)_2$~~,~~; $(CF_2CF_2SO_3^-)_2$~~,~~; $(CF_3SO_2^-)_2N^-$~~,~~ ~~-~~; $CF_3CF_2(CF_3)_2CO^-$~~,~~ ~~-~~; $(CF_3SO_2^-)_2CH^-$~~,~~ ~~-~~; $(SF_5)_3C^-$~~,~~ ~~-~~; $(CF_3SO_2)_3C^-$~~,~~ ~~-~~; $[O(CF_3)_2C_2(CF_3)_2O]_2PO^-$~~,~~ ~~-~~; $(CF_3(CF_2)_7\ SO_3^-$~~,~~ ~~-~~; and mixtures thereof~~; and.~~

~~(II) wherein the polymer host is selected from the group consisting essentially of homopolymers and copolymers of polyolefins, polystyrenes, polyvinyls, polyacrylics, polyhalo-olefins, polydienes, polyoxides/esthers/acetals, polysulfides, polyesters/thioesters, polyamides/thioamides, polyurethanes/thiourethanes, polyureas/thioureas, polyimides/thioimides, polyanhydrides/thianhydrides, polycarbonates/thiocarbonates, polyimines, polysiloxanes/silanes, polyphosphazenes, polyketones/thioketones, polysulfones/sulfoxides/sulfonates/sulfoamides, polyphylenes, and mixtures thereof.~~

7. The electrochemical energy storage device of claim 5, wherein the electrolyte material further comprises an inorganic filler, and wherein at least most of the inorganic filler comprises particles having a surface area of at least about $10m^2/g$, a maximum dimension of about 50 micrometers, and an average pore size of less than about 10 micrometers.

8. The electrochemical energy storage device of claim 5, further comprising a polymer host, wherein the polymer host is selected from the group of polymers consisting of homopolymers and copolymers of polyolefins, polystyrenes, polyvinyls, polyacrylics, polyhalo-olefins, polydienes, polyoxides/esthers/acetals, polysulfides, polyesters/thioesters, polyamides/thioamides, polyurethanes/thiourethanes, polyureas/thioureas, polyimides/thioimides, polyanhydrides/thianhydrides, polycarbonates/thiocarbonates, polyimines, polysiloxanes/silanes, polyphosphazenes, polyketones/thioketones, polysulfones/sulfoxides/sulfonates/sulfoamides, polyphylenes, and mixtures thereof and wherein the ionic liquid and polymer host form a self-supporting film.

~~7. The ultracapacitor of claim 5, wherein the electrolyte material further comprises an inorganic filler, wherein at least most of the filler particles have a surface area of at least about 10 m^2/g, a maximum dimension of about 50 micrometers, and an average pore size of less than about 10 micrometers.~~

~~8.~~9. An ~~ultracapacitor~~electrochemical energy storage device, comprising:

(a) first and second electrodes comprising etched carbon nanotubes having amorphous carbon covering the carbon nanotube surface removed, opposing first and second ends, and an interior surface; ~~and~~

(b) an electrolyte material comprising an ionic liquid, and

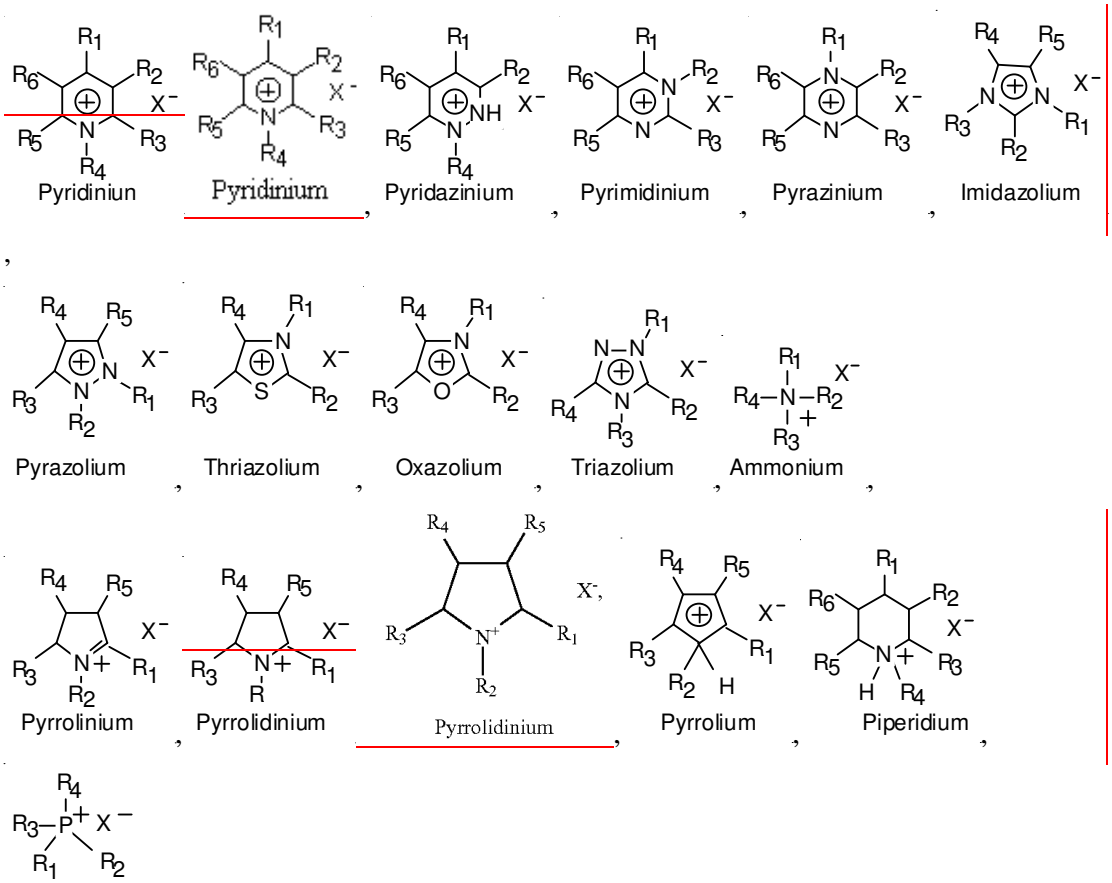
(c) a solid-phase electrolyte material comprising ~~an ionic liquid and~~ a polymer host~~, the polymer host forming a self-supporting film comprising~~ and the ionic liquid, wherein at least most of the first ends of one or both of the first and second electrodes are open to permit the electrolyte material to access the interior surfaces of the etched carbon nanotubes and in contact with the electrolyte material.

~~9~~10. The ~~ultracapacitor~~ electrochemical energy storage device of claim ~~8~~9, wherein the ionic liquid has a melting point of no more than about 100 degrees Celsius, a decomposition temperature of at least about 200 degrees Celsius, a viscosity of no more than about 200 Cp, an ionic conductivity of at least about 0.1mS/cm, and an electrochemical window of at least about 2 Volts.

~~10~~11. The ~~ultracapacitor~~ electrochemical energy storage device of claim ~~9~~10, wherein~~:~~

~~(I)~~ the ionic liquid comprises:

(A) at least one cation selected from the group of cations consisting ~~essentially~~ of the following compounds and mixtures thereof:



wherein R_1, R_2, R_3, R_4, R_5, and R_6 of the cationic components are identical or different and are selected from the group consisting ~~essentially~~ of:

(i) a hydrogen;

(ii) a halogen;

(iii) a hydroxyl;

(iv) an amine;

(v) a thiol;

(vi) a C_1 to C_{25} straight-chain~~,~~ or branched aliphatic hydrocarbon radical;

(vii) a C_5 to C_{30} cycloaliphatic hydrocarbon radical;

(viii) a C_6 to C_{30} aromatic hydrocarbon radical;

(ix) a C_7 to C_{40} alkylaryl radical;

(x) a C_2 to C_{25} linear or branched aliphatic hydrocarbon radical having interruption by one or more heteroatoms, such as, oxygen, nitrogen or sulfur;

(xi) a C_2 to C_{25} linear or branched aliphatic hydrocarbon radical having interruption by one or more functionalities selected from the group of aliphatic hydrocarbons consisting ~~essentially~~ of:

(a') a carbonyl;

(b') an ester;

(c') an amide, where R' is selected from the group consisting ~~essentially~~ of hydrogen, C_1-C_{12} straight-chain, branched or cyclic alkane or alkene;

(d') a sulfonate;

(e') a sulfonamide, where R' is selected from the group consisting ~~essentially~~ of hydrogen, C_1-C_{12} straight-chain, branched or cyclic alkane or alkene;

(xii) a C_2 to C_{25} linear or branched aliphatic hydrocarbon radical terminally functionalized by Cl, Br, F, I, NH, OH, NH_2, $NHCH_3$ or SH;

(xiii) a C_5 to C_{30} cycloaliphatic hydrocarbon radical having at least one heteroatom selected from the group of hydrocarbon radials consisting ~~essentially~~ of O, N, S, and optionally substituted with at least one of the following Cl, Br, F, I, NH, OH, NH_2, $NHCH_3$ or SH;

(xiv) a C_7 to C_{40} alkylaryl radical having at least one heteroatom selected from the group heteroatoms consisting ~~essentially~~ of O, N, S, and optionally substituted with at least one of the following:

(a'') a C_2 to C_{25} straight-chain~~,~~ or branched hydrocarbon radical substituted with at least one of the following Cl, Br, F, I, NH, OH, NH_2, $NHCH_3$ or SH;

(b'') a C_5 to C_{30} cycloaliphatic hydrocarbon radical substituted with at least one of the following Cl, Br, F, I, NH, OH, NH_2, $NHCH_3$ or SH

(c'') a hydroxyl;

(d'') an amine;

(e'') a thiol;

(xv) a polyether of the type $-O-(-R_7-O-)_n-R_8$ or block or random type $-O-(-R_7-O-)_n-(-R_{7'}-O-)_m-R_8$,wherein at least one of the following is true:

(a''') R_7 is a linear or branched hydrocarbon radical having from 2 to 4 carbon atoms;

(b''') $R_{7'}$ is a linear or branched hydrocarbon radical having from 2 to 4 carbon atoms; and

(c''') wherein n is from 1 to 40; and

(d''') R_8 is hydrogen, or a C_5 to C_{30} straight-chain or branched hydrocarbon radical, or a C_5 to C_{30} cycloaliphatic hydrocarbon radical, or a C_6 to C_{30} aromatic hydrocarbon radical, or a C_7 to C_{40} alkylaryl radical; and

(xvi) a polyether of the type $-O-(-R_7-O-)_n-C(O)-R_8$ or block or random type $-O-(-R_7-O-)_n-(-R_{7'}-O-)_m-C(O)-R_8$,wherein at least of the following is true:

(a'''') R_7 is a linear or branched hydrocarbon radical having from 2 to 4 carbon atoms;

(b'''') $R_{7'}$ is a linear or branched hydrocarbon radical having from 2 to 4 carbon atoms; and

(c'''') wherein n is from 1 to 40; and

(d'''') R_8 is hydrogen, or a C_5 to C_{30} straight-chain or branched hydrocarbon radical, or a C_5 to C_{30} cycloaliphatic hydrocarbon radical, or a C_6 to C_{30} aromatic hydrocarbon radical, or a C_7 to C_{40} alkylaryl radical; and

(B) at least one anion selected from the group of anions consisting ~~essentially~~ of F^-; Cl^-, Br^-; I^-; NO_3^-; $N(CN)_2^-$; BF_4^-; ClO_4^-; PF_6^-; RSO_3^-; $RCOO^-$; where R is an alkyl group, substituted alkyl group, or phenyl group; $(CF_3)_2PF_4^-$, $(CF_3)_3PF_3^-$, $(CF_3)_4PF_2^-$, $(CF_3)_5PF^-$, $(CF_3)_6P^-$, $(CF_2SO_3^-)_2$, $(CF_2CF_2SO_3^-)_2$, $(CF_3SO_2^-)_2N^-$, $CF_3CF_2(CF_3)_2CO^-$, $(CF_3SO_2^-)_2CH^-$, $(SF_5)_3C^-$, $(CF_3SO_2)_3C^-$, $[O(CF_3)_2C_2(CF_3)_2O]_2PO^-$, $(CF_3(CF_2)_7SO_3^-$, and mixtures thereof~~; and~~.

~~(II)~~12. The electrochemical energy storage device of claim 10, wherein the polymer host is selected from the group of polymers consisting ~~essentially~~ of homopolymers and copolymers of polyolefins, polystyrenes, polyvinyls, polyacrylics, polyhalo-olefins, polydienes, polyoxides/esthers/acetals, polysulfides, polyesters/thioesters, polyamides/thioamides, polyurethanes/thiourethanes, polyureas/thioureas, polyimides/thioimides, polyanhydrides/thianhydrides, polycarbonates/thiocarbonates, polyimines, polysiloxanes/silanes, polyphosphazenes, polyketones/thioketones, polysulfones/sulfoxides/sulfonates/sulfoamides, polyphylenes, and mixtures thereof and wherein the ionic liquid and polymer host form a self-supporting film.

13. The electrochemical energy storage device of claim 12, wherein a molar ratio of ionic liquid to polymer host ranges from about 0.1:1 to about 10:1.

14. The electrochemical energy storage device of claim 9, wherein the solid-phase electrolyte material comprises a substantially nonconductive, inorganic filler, and wherein at least most of the nonconductive, inorganic filler comprises particles having a surface area of at least about 10 m^2/g, a maximum dimension of about 50 micrometers, and an average pore size of less than about 10 micrometers.

15. The electrochemical energy storage device of claim 9, wherein the carbon nanotubes have an interior diameter, wherein the ionic liquid comprises cations and anions, wherein the anions and/or cations have a size sufficiently less than the interior diameter, and wherein the opened first ends permit the anions and/or cations to access the interior surfaces of the nanotubes.

16. The electrochemical energy storage device of claim 15, wherein at least most of the etched carbon nanotubes of the first and second electrodes are aligned carbon nanotubes, wherein the aligned carbon nanotubes on the first and second electrodes are substantially parallel to one another along substantially the entire length of the etched carbon nanotubes, and wherein the cations comprise at least one of pyridinium, pyridazinium, pyrimidinium, pyrazinium, imidazolium, pyrazolium, thiazolium, oxazolium, triazolium, ammonium, pyrrolidinium, pyrrolinium, pyrrolium, and piperidinium.

17. An electrochemical energy storage device, comprising:

(a) first and second electrodes, the first and second electrodes being oppositely charged electrodes and having primarily comprising substantially aligned carbon nanotubes, wherein the aligned carbon nanotubes have opposing first and second ends; and

(b) an electrolyte material, comprising oppositely charged ions, in contact with at least most of the first ends of the carbon nanotubes of the first and second electrodes, wherein at least one of the first ends are open to permit the charged ions to access an interior surface of the corresponding nanotube, wherein the charged ions have a size less than interior diameters of the corresponding carbon nanotube, wherein the electrolyte material comprises an ionic liquid having a melting point of no more than about 100 degrees Celsius, a decomposition temperature of at least about 200 degrees Celsius, a viscosity of no more than about 200 Cp, an ionic conductivity of at least about 0.1 mS/cm, and an electrochemical window of at least about 2 Volts and wherein the electrolyte material further comprises an inorganic filler, wherein inorganic filler comprises particles having a surface area of at least about 10 m^2/g, a maximum dimension of about 50 micrometers, and an average pore size of less than about 10 micrometers.

18. An electrochemical energy storage device, comprising:

(a) first and second electrodes comprising etched carbon nanotubes having amorphous carbon layer covering the carbon nanotube surface removed;

(b) a solid-phase electrolyte material comprising an ionic liquid, wherein the ionic liquid has a melting point of no more than about 100 degrees Celsius, a decomposition temperature of at least about 200 degrees Celsius, a viscosity of no more than about 200 Cp, an ionic conductivity of at least about 0.1 mS/cm, and an electrochemical window of at least about 2 Volts; and

a polymer host selected from the group of polymers consisting of homopolymers and copolymers of polyolefins, polystyrenes, polyvinyls, polyacrylics, polyhalo-olefins, polydienes, polyoxides/esthers/acetals, polysulfides, polyesters/thioesters, polyamides/thioamides, polyurethanes/thiourethanes, polyureas/thioureas, polyimides/thioimides, polyanhydrides/thianhydrides, polycarbonates/thiocarbonates, polyimines, polysiloxanes/silanes, polyphosphazenes, polyketones/thioketones, polysulfones/sulfoxides/sulfonates/sulfoamides, polyphylenes, and mixtures thereof, wherein the ionic liquid and polymer host forms a self-supporting film.

19. An electrochemical energy storage device, comprising:

(a) first and second electrodes comprising etched carbon nanotubes;

(b) a solid-phase electrolyte material comprising an ionic liquid, wherein the ionic liquid has a melting point of no more than about 100 degrees Celsius, a decomposition temperature of at least about 200 degrees Celsius, a viscosity of no more than about 200 Cp, an ionic conductivity of at least about 0.1 mS/cm, and an electrochemical window of at least about 2 Volts; and

a polymer host, wherein the solid-phase electrolyte material comprises a substantially nonconductive, inorganic filler, and wherein the ononconductive, inorganic filler comprises particles having a surface area of at least about 10 m^2/g, a maximum dimension of about 50 micrometers, and an average pore size of less than about 10 micrometer.

20. An electrochemical energy storage device, comprising:

(a) first and second electrodes, the first and second electrodes are oppositely charged and primarily comprise substantially aligned carbon nanotubes, the aligned carbon nanotubes have opposing first and second ends; and

(b) an electrolyte material, comprising ions, in contact with at least most of the first ends of the aligned carbon nanotubes of the first and second electrodes, wherein at least one of the first ends in contact with the electrolyte material is open to permit the ions to access an interior surface of the corresponding nanotube, wherein the ions comprise anions and cations, wherein the cations comprise at least one of pyridinium, pyridazinium, pyrimidinium, pyrazinium, imidazolium, pyrazolium, thiazolium, oxazolium, triazolium, ammonium, pyrrolidinium, pyrrolinium, pyrrolium, and piperidinium.

21. An electrochemical energy storage device, comprising:

(a) first and second electrodes comprising etched carbon nanotubes having opposing first and second ends and an interior diameter, wherein at least most of the first ends of one or both of the first and second electrodes are open; and

(b) a solid-phase electrolyte material comprising a polymer host and an ionic liquid, wherein at least most of the open first ends are in contact with the electrolyte material, wherein the electrolyte material comprises anions and cations having has a size less than the interior diameter.

~~11. The ultracapacitor of claim 9, wherein the polymer host is selected from the group consisting essentially of homopolymers and copolymers of polyolefins, polystyrenes, polyvinyls, polyacrylics, polyhalo-olefins, polydienes, polyoxides/esthers/acetals, polysulfides, polyesters/thioesters, polyamides/thioamides, polyurethanes/thiourethanes, polyureas/thioureas, polyimides/thioimides, polyanhydrides/thianhydrides, polycarbonates/thiocarbonates, polyimines, polysiloxanes/silanes, polyphosphazenes, polyketones/thioketones, polysulfones/sulfoxides/sulfonates/sulfoamides, polyphylenes, and mixtures thereof.~~

~~12. The ultracapacitor of claim 8, wherein the solid-phase electrolyte material comprises a substantially nonconductive, inorganic filler, wherein at least most of the filler particles have a surface area of at least about 10 m^2/g, a maximum dimension of about 50 micrometers, and an average pore size of less than about 10 micrometers.~~

~~13. The ultracapacitor of claim 8, wherein a molar ratio of ionic liquid to polymer host ranges from about 0.1:1 to about 10:1.~~

~~14. The ultracapacitor of claim 8, wherein the first and second carbon-based electrodes are primarily comprised of carbon nanotubes, wherein at least most of the first ends of the carbon nanotubes are open to permit the ions to access interior surfaces of the nanotubes, and wherein the sizes of the cations and anions in the ionic liquid are less than interior diameters of the carbon nanotubes.~~

~~15. The ultracapacitor of claim 14, wherein at least most of the carbon nanotubes are aligned carbon nanotubes.~~

~~16. A method, comprising:~~

~~(a) contacting a polymer host with an organic solvent to form a first composition;~~

~~(b) contacting an ionic liquid with the first composition; and~~

~~(c) removing at least most of the organic solvent from the first composition to form a free-standing film comprising the polymer host and ionic liquid.~~

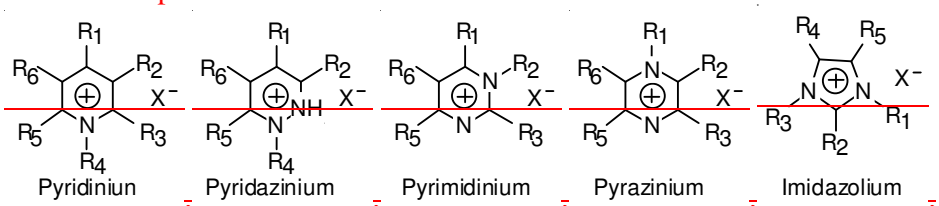
~~17. The method of claim 16, wherein the polymer host is dissolved substantially in the first composition, wherein the organic solvent is removed from the first composition by heating the first composition to a selected temperature under a~~

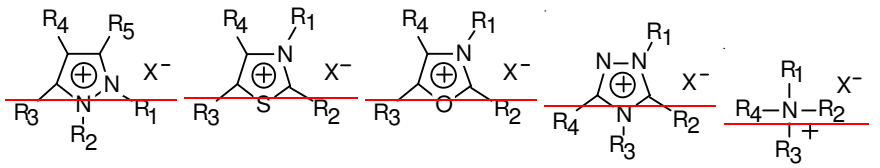
vacuum, wherein the selected temperature is higher than a boiling point of the solvent but lower than decomposition temperatures of the ionic liquid and polymer host, and wherein the first composition is spread onto a substrate during step (c).

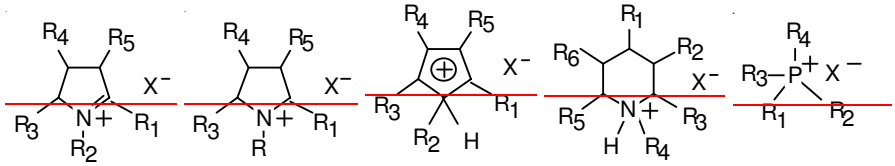
18. The method of claim 16, wherein:

(I) the ionic liquid comprises:

(A) at least one cation selected from the group consisting essentially of the following compounds and mixtures thereof:







wherein R_1, R_2, R_3, R_4, R_5, and R_6 of the cationic components are identical or different and are selected from the group consisting essentially of:

(i) a hydrogen;

(ii) a halogen;

(iii) a hydroxyl;

(iv) an amine;

(v) a thiol;

(vi) a C_1 to C_{25} straight chain, branched aliphatic hydrocarbon radical;

(vii) a C_5 to C_{30} cycloaliphatic hydrocarbon radical;

(viii) a C_6 to C_{30} aromatic hydrocarbon radical;

(ix) a C_7 to C_{40} alkylaryl radical;

(x) a C_2 to C_{25} linear or branched aliphatic hydrocarbon radical having interruption by one or more heteroatoms, such as, oxygen, nitrogen or sulfur;

(xi) a C_2 to C_{25} linear or branched aliphatic hydrocarbon radical having interruption by one or more functionalities selected from the group consisting essentially of:

(a') a carbonyl;

(b') an ester;

(c') an amide, where R' selected from the group consisting essentially of hydrogen, C_1-C_{12} straight-chain, branched or cyclic alkane or alkene;

(d') a sulfonate;

(e') a sulfonamide, where R' selected from the group consisting essentially of hydrogen, C_1-C_{12} straight-chain, branched or cyclic alkane or alkene;

(xii) a C_2 to C_{25} linear or branced aliphatic hydrocarbon radical terminally functionalized by Cl, Br, F, I, NH, OH, NH_2, $NHCH_3$ or SH;

(xiii) a C_5 to C_{30} cycloaliphatic hydrocarbon radical having at least one heteroatom selected from the group consisting essentially of O, N, S, and optionally substituted with at least one of the following Cl, Br, F, I, NH, OH, NH_2, $NHCH_3$ or SH;

(xiv) a C_7 to C_{40} alkylaryl radical heteroatom selected from the group consisting essentially of O, N, S, and optionally substituted with at least one of the following:

(a'') a C_2 to C_{25} straight-chain, branched hydrocarbon radical substituted with at least one of the following Cl, Br, F, I, NH, OH, NH_2, $NHCH_3$ or SH;

(b'') a C_5 to C_{30} cycloaliphatic hydrocarbon radical substituted with at least one of the following Cl, Br, F, I, NH, OH, NH_2, $NHCH_3$ or SH

(c'') a hydroxyl;

(d'') an amine;

(e'') a thiol;

(xv) a polyether of the type $-O-(-R_7-O-)_n-R_8$ or block or random type $-O-(-R_7-O-)_n-(-R_{7'}-O-)_m-R_8$,wherein at least of the following is true:

(a''') R_7 is a linear or branched hydrocarbon radical having from 2 to 4 carbon atoms;

(b''') $R_{7'}$ is a linear or branched hydrocarbon radical having from 2 to 4 carbon atoms; and

(c''') wherein n is from 1 to 40; and

(d''') R_8 is hydrogen, or a C_5 to C_{30} straight-chain or branched hydrocarbon radical, or a C_5 to C_{30}cycloaliphatic hydrocarbon radical, or a C_6 to C_{30} aromatic hydrocarbon radical, or a C_7 to C_{40} alkylaryl radical; and

(xvi) a polyether of the type $-O-(-R_7-O-)_n-C(O)-R_8$ or block or random type $-O-(-R_7-O-)_n-(-R_{7'}-O-)_m-C(O)-R_8$,wherein at least of the following is true:

(a'''') R_7 is a linear or branched hydrocarbon radical having from 2 to 4 carbon atoms;

(b'''') $R_{7'}$ is a linear or branched hydrocarbon radical having from 2 to 4 carbon atoms; and

(c'''') wherein n is from 1 to 40; and

(d'''') R_8 is hydrogen, or a C_5 to C_{30} straight chain or branched hydrocarbon radical, or a C_5 to C_{30} cycloaliphatic hydrocarbon radical, or a C_6 to C_{30} aromatic hydrocarbon radical, or a C_7 to C_{40} alkylaryl radical; and

(B) at least one anion selected from the group consisting essentially of F^-; Cl^-, Br^-; I^-; NO_3^-; $N(CN)_2^-$; BF_4^-; ClO_4^-; PF_6^-; RSO_3^-; $RCOO^-$; where R is an alkyl group, substituted alkyl group, or phenyl group; $(CF_3)_2PF_4^-$, $(CF_3)_3PF_3^-$, $(CF_3)_4PF_2^-$, $(CF_3)_5PF^-$, $(CF_3)_6P^-$, $(CF_2SO_3^-)_2$, $(CF_2CF_2SO_3^-)_2$, $(CF_3SO_2^-)_2N^-$, $CF_3CF_2(CF_3)_2CO^-$, $(CF_3SO_2^-)_2CH^-$, $(SF_5)_3C^-$, $(CF_3SO_2)_3C^-$, $[O(CF_3)_2C_2(CF_3)_2O]_2PO^-$, $(CF_3(CF_2)_7SO_3^-$, and mixtures thereof; and

(II) wherein the polymer host is selected from the group consisting essentially of homopolymers and copolymers of polyolefins, polystyrenes, polyvinyls, polyacrylics, polyhalo-olefins, polydienes, polyoxides/esthers/acetals, polysulfides, polyesters/thioesters, polyamides/thioamides, polyurethanes/thiourethanes, polyureas/thioureas, polyimides/thioimides, polyanhydrides/thianhydrides, polycarbonates/thiocarbonates, polyimines, polysiloxanes/silanes, polyphosphazenes, polyketones/thioketones, polysulfones/sulfoxides/sulfonates/sulfoamides, polyphylenes, and mixtures thereof.

19. The method of claim 16, wherein the ionic liquid has a melting point of no more than about 100 degrees Celsius, a decomposition temperature of at least about 200 degrees Celsius, a viscosity of no more than about 200 Cp, an ionic conductivity of at least about 0.1 mS/cm, and an electrochemical window of at least about 2 Volts.

20. The method of claim 16, wherein in step (b) the first composition further comprises a substantially nonconductive, inorganic filler and wherein at least most of the filler particles have a surface area of at least about 10 m^2/g, a maximum dimension of about 50 micrometers, and an average pore size of less than about 10 micrometers.

21. A method, comprising:

(a) first forming a self-supporting polymer film comprising a host polymer;

(b) second contacting the film with an ionic liquid; and

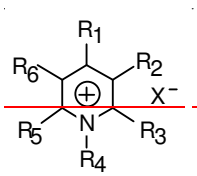
(c) heating the film and ionic liquid, while in contact with one another, to a selected temperature above a glass transition temperature of the polymer host but below decomposition temperatures of the ionic liquid and polymer host to impregnate the polymer film with the ionic liquid.

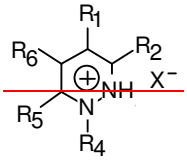
22. The method of claim 21, wherein the self-supporting polymer film comprises a substantially nonconductive, inorganic filler and wherein at least most of the filler particles have a surface area of at least about 10 m^2/g, a maximum dimension of about 50 micrometers, and an average pore size of less than about 10 micrometers.

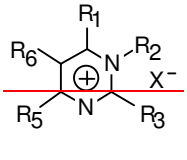
23. The method of claim 21, wherein:

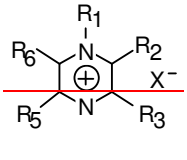
(I) the ionic liquid comprises:

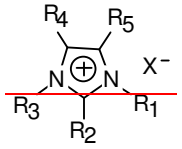
(A) at least one cation selected from the group consisting essentially of the following compounds and mixtures thereof:

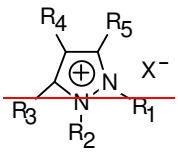

Pyridinium ;

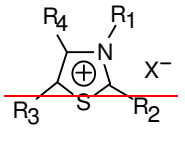

Pyridazinium ;

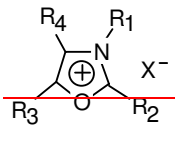

Pyrimidinium ;

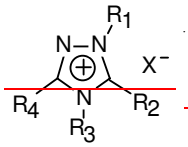

Pyrazinium ;

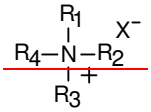

Imidazolium ;

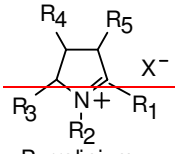

Pyrazolium ;

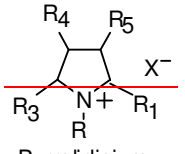

Thriazolium ;

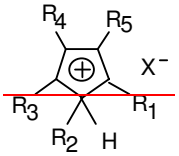

Oxazolium ;

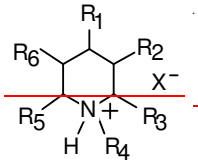

Triazolium ;

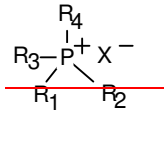

Ammonium ;


Pyrrolinium ;


Pyrrolidinium ;


Pyrrolium ;


Piperidium ;


Phosphonium ;

~~wherein R_1, R_2, R_3, R_4, R_5, and R_6 of the cationic components are identical or different and are selected from the group consisting essentially of:~~

~~(i) a hydrogen;~~

~~(ii) a halogen;~~

~~(iii) a hydroxyl;~~

~~(iv) an amine;~~

~~(v) a thiol;~~

~~(vi) a C_1 to C_{25} straight-chain, branched aliphatic hydrocarbon radical;~~

~~(vii) a C_5 to C_{30} cycloaliphatic hydrocarbon radical;~~

~~(viii) a C_6 to C_{30} aromatic hydrocarbon radical;~~

~~(ix) a C_7 to C_{40} alkylaryl radical;~~

~~(x) a C_2 to C_{25} linear or branched aliphatic hydrocarbon radical having interruption by one or more heteroatoms, such as, oxygen, nitrogen or sulfur;~~

~~(xi) a C_2 to C_{25} linear or branched aliphatic hydrocarbon radical having interruption by one or more functionalities selected from the group consisting essentially of:~~

~~(a') a carbonyl;~~

~~(b') an ester;~~

~~(c') an amide, where R' selected from the group consisting essentially of hydrogen, C_1-C_{12} straight-chain, branched or cyclic alkane or alkene;~~

~~(d') a sulfonate;~~

~~(e') a sulfonamide, where R' selected from the group consisting essentially of hydrogen, C_1-C_{12} straight-chain, branched or cyclic alkane or alkene;~~

~~(xii) a C_2 to C_{25} linear or branched aliphatic hydrocarbon radical terminally functionalized by Cl, Br, F, I, NH, OH, NH_2, $NHCH_3$ or SH;~~

(xiii) a C_5 to C_{30} cycloaliphatic hydrocarbon radical having at least one heteroatom selected from the group consisting essentially of O, N, S, and optionally substituted with at least one of the following Cl, Br, F, I, NH, OH, NH_2, $NHCH_3$ or SH;

(xiv) a C_7 to C_{40} alkylaryl radical heteroatom selected from the group consisting essentially of O, N, S, and optionally substituted with at least one of the following:

(a'') a C_2 to C_{25} straight chain, branched hydrocarbon radical substituted with at least one of the following Cl, Br, F, I, NH, OH, NH_2, $NHCH_3$ or SH;

(b'') a C_5 to C_{30} cycloaliphatic hydrocarbon radical substituted with at least one of the following Cl, Br, F, I, NH, OH, NH_2, $NHCH_3$ or SH

(c'') a hydroxyl;

(d'') an amine;

(e'') a thiol;

(xv) a polyether of the type $-O-(-R_7-O-)_n-R_8$ or block or random type $-O-(-R_7-O-)_n-(-R_{7'}-O-)_m-R_8$,wherein at least of the following is true:

(a''') R_7 is a linear or branched hydrocarbon radical having from 2 to 4 carbon atoms;

(b''') $R_{7'}$ is a linear or branched hydrocarbon radical having from 2 to 4 carbon atoms; and

(c''') wherein n is from 1 to 40; and

(d''') R_8 is hydrogen, or a C_5 to C_{30} straight chain or branched hydrocarbon radical, or a C_5 to C_{30}cycloaliphatic hydrocarbon radical, or a C_6 to C_{30} aromatic hydrocarbon radical, or a C_7 to C_{40} alkylaryl radical; and

(xvi) a polyether of the type $-O-(-R_7-O-)_n-C(O)-R_8$ or block or random type $-O-(-R_7-O-)_n-(-R_{7'}-O-)_m-C(O)-R_8$,wherein at least of the following is true:

(a'''') R_7 is a linear or branched hydrocarbon radical having from 2 to 4 carbon atoms;

(b'''') $R_{7'}$ is a linear or branched hydrocarbon radical having from 2 to 4 carbon atoms; and

(c'''') wherein n is from 1 to 40; and

(d'''') R_8 is hydrogen, or a C_5 to C_{30} straight chain or branched hydrocarbon radical, or a C_5 to C_{30}cycloaliphatic hydrocarbon radical, or a C_6 to C_{30} aromatic hydrocarbon radical, or a C_7 to C_{40} alkylaryl radical; and

(B) at least one anion selected from the group consisting essentially of F^-; Cl^-, Br^-; I^-; NO_3^-; $N(CN)_2^-$; BF_4^-; ClO_4^-; PF_6^-; RSO_3^-; $RCOO^-$; where R is an alkyl group, substituted alkyl group, or phenyl group; $(CF_3)_2PF_4^-$, $(CF_3)_3PF_3^-$, $(CF_3)_4PF_2^-$, $(CF_3)_5PF^-$, $(CF_3)_6P^-$, $(CF_2SO_3^-)_2$, $(CF_2CF_2SO_3^-)_2$, $(CF_3SO_2^-)_2N^-$, $CF_3CF_2(CF_3)_2CO^-$, $(CF_3SO_2^-)_2CH^-$, $(SF_5)_3C^-$, $(CF_3SO_2)_3C^-$, $[O(CF_3)_2C_2(CF_3)_2O]_2PO^-$, $(CF_3(CF_2)_7SO_3^-$, and mixtures thereof; and

~~(II) wherein the polymer host is selected from the group consisting essentially of homopolymers and copolymers of polyolefins, polystyrenes, polyvinyls, polyacrylics, polyhalo-olefins, polydienes, polyoxides/esthers/acetals, polysulfides, polyesters/thioesters, polyamides/thioamides, polyurethanes/thiourethanes, polyureas/thioureas, polyimides/thioimides, polyanhydrides/thianhydrides, polycarbonates/thiocarbonates, polyimines, polysiloxanes/silanes, polyphosphazenes, polyketones/thioketones, polysulfones/sulfoxides/sulfonates/sulfoamides, polyphylenes, and mixtures thereof.~~