

Composite Materials

Technical Field

The present invention generally relates to composite materials. The composite materials are useful in electrochromic devices. The present invention also relates to a method of preparing said composite materials and electrochromic devices.

Background Art

Optoelectronics is an emerging field where electrochromic materials and devices have increasingly showed great potential and have been used in various applications, such as in electronic billboards, mirrors and displays, smart glass, wearable and portable electronics, energy-storage devices, light-emitting electrochemical cells, and many others. Despite its widespread use and various advantages, there still exists several challenges in the application of the materials and devices in terms of their properties, durability, lifetime, performance of the electrochromic materials and devices and the method of preparation of the electrochromic materials and devices.

Electrochromic devices (ECDs) change optical properties (i.e., transmission, absorption, or reflectance) when a voltage is applied. Its working principle is applied in composite materials and electrochromic devices to enable the display and presentation of information and content. Composite materials which can be commonly used as electrolytes in an ECD is indispensable as it hosts essential ions for electrochromic reaction and balances residual charges, which influence the switching performance.

Conventional liquid electrolytes, such as aqueous or low-volatility organic solvents, though possessing high ionic conductivities, are severely affected by evaporation and leakage issues. As a result, the lifetime of an ECD of a conventional liquid electrolyte, is significantly shortened due to electrolyte evaporation, which is unavoidable when aqueous or low-volatility organic solvent is used. Furthermore, the seepage of electrolytes is another key issue that needs to be addressed as it would lead to safety concerns and a decrease in the electrochemical performance.

Hence, there is a need to provide a composite material and/or electrochromic device that overcomes, or at least ameliorates, one or more of the disadvantages described above. Furthermore, other desirable features and characteristics will become apparent from the subsequent detailed description and the appended claims,

taken in conjunction with the accompanying figures and this background of the disclosure.

Summary

According to the present disclosure, there is provided a composite material comprising:

an ionic liquid A; and

a polymer matrix comprising a network of crosslinked poly(ionic liquid B).

According to a first aspect of the present disclosure, there is provided an electrochromic device comprising an electrolyte sandwiched between two electrodes, the electrolyte comprising a composite material comprising:

an ionic liquid A, wherein the ionic liquid A is 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (EMIMTFSI); and

a polymer matrix comprising a network of crosslinked poly(ionic liquid B), wherein the polymer matrix is formed by reaction of an ionic liquid B with a crosslinking agent, wherein the ionic liquid B is 1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl) imide (BVIMTFSI), and the crosslinking agent is poly(ethylene glycol) diacrylate (PEGDA).

Advantageously, the composite materials are in a solid state or immobilized, and are thus non-volatile (i.e., do not evaporate) and do not leak and/or seep. Furthermore, the composite materials are flexible and/or deformable with low glass transition temperature (T_g) and modulus. The composite materials are advantageously stable with long lifetime, durable and do not pose any safety concerns.

Also advantageously, the composite materials are highly transparent in visible and part of near-infrared region (i.e., 380 nm to 1250 nm). This allows the composite material to be used for various applications such as electrochromic devices.

Advantageously, the polymer matrix may comprise chemicals with similar structures as well as compatibilized polarity and solubility. This advantageously results in a homogenized polymer matrix where the chemicals in the polymer matrix are miscible with one another and form a single phase. Furthermore, the chemicals in the polymer matrix may advantageously remain miscible with one another during temperature changes such that there is no phase separation occurring in the polymer matrix when temperature changes. This temperature independence means that the composite materials of the present invention do not undergo phase changes with temperature variations. The composite materials may remain stable and do not experience phase separation or aggregation. This advantage can be attributed to the presence of electrostatic interactions between the ionic liquid and the polymer matrix. These interactions

stabilize the composite material and prevent phase separation or aggregation at different temperatures which make them excellent materials for electrochromic devices. The advantage of having a homogenized polymer matrix is that it improves the structural integrity of the composite material by having a consistent distribution of components within the polymer matrix which helps distribute stress and load evenly across the polymer matrix. This reduces the likelihood of localized weak points or areas prone to failure. Furthermore, a homogenized polymer matrix ensures a uniform performance across the composite material.

Further advantageously, the composite materials comprise ionic liquids, which possess remarkable thermal/chemical stability, non-volatility, and good conductivity

in solid state. As a result, the composite materials possess excellent physicochemical stability, including thermal stability (from -20 °C to 100 °C), electrochemical stability, and air stability, allowing them to perform in various conditions and applications.

Even more advantageously, the composite materials exhibit high ionic conductivity in the region of mS/cm, allowing good electrochemical and electrochromic performance (in terms of optical modulation, response time, stability) with either organic or inorganic electrochromic materials. Hence, the composite materials may be utilized as solid-state composite materials for electrochromic applications due to its high ionic conductivity with promising thermal and electrochemical stability.

According to the present disclosure, there is provided a method of preparing a composite material as disclosed herein, comprising the steps of:

- (i) preparing a mixture of ionic liquid A, ionic liquid B, crosslinking agent, and a photoinitiator;
- (ii) curing the mixture with light irradiation,

wherein the crosslinking agent reacts with ionic liquid B to form a polymer matrix comprising a network of crosslinked poly(ionic liquid B).

Advantageously, the disclosed method enables the preparing of composite materials in less than a minute under ambient conditions. The disclosed method is fast, simple and easy to perform. Furthermore, the materials required for the method are inexpensive and easy to obtain.

According to the present disclosure, there is provided an electrochromic device comprising an electrolyte sandwiched between two electrodes, wherein the electrolyte comprises the composite material as disclosed herein.

Advantageously, benefitting from the properties of the composite material, the assembled electrochromic device may display high colour contrast and fast response time with good endurance over thousands of switching cycles and exhibit great performance as an electrochromic device. The composite materials of the present invention may display colour-switching properties in response to changes in temperature or changes in applied current/potential while still retaining its state and form. Further advantageously, distorting or twisting the composite material does not have an effect on its ability to colour-switch. The composite materials may turn from a transparent state to a transmissive coloured state which still allows for partial visualization. This advantageously allows the composite materials of the present disclosure to be used in applications where changing coloured states and partial visualization are important, such as in optical applications (e.g. sunglasses, protective eye wears and lenses and window films. For instance, having partial visualization in architectural windows in buildings can balance natural light, allowing occupants to enjoy the view outside while maintaining a level of shielding from excessive sunlight. In addition, complete blockage of light or

visibility may not be suitable for specific industries, such as aircraft windows, due to safety reasons.

Also advantageously, the composite materials show good compatibility when coupled with deformable substrates (like ultra-thin indium doped tin oxide (ITO) glass, conductive textile, and indium-doped tin oxide polyethylene terephthalate (ITO-PET) substrate) to form and realize electrochromic devices such as flexible electrochromic eye protector and display applications.

According to the present disclosure, there is provided a method of forming an electrochromic device comprising:

- (i) applying a mixture of ionic liquid A, ionic liquid B, crosslinking agent, a photoinitiator, and optionally a metal borate complex between two electrodes; and
- (ii) curing the mixture with light irradiation,

wherein the crosslinking agent reacts with ionic liquid B to form a polymer matrix comprising a network of crosslinked poly(ionic liquid B).

According to a further aspect of the present disclosure, there is provided a method of forming an electrochromic device comprising:

- (i) applying a mixture of ionic liquid A, ionic liquid B, crosslinking agent, a photoinitiator, and optionally a metal borate complex between two electrodes; and
- (ii) curing the mixture with light irradiation,

wherein the crosslinking agent reacts with ionic liquid B to form a polymer matrix comprising a network of crosslinked poly(ionic liquid B); and

wherein the ionic liquid A is 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (EMIMTFSI), the ionic liquid B is 1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl) imide (BVIMTFSI), and the crosslinking agent is poly(ethylene glycol) diacrylate (PEGDA).

Advantageously, the disclosed method to form an electrochromic device is a rapid in-situ polymerization method, which is performed under ambient conditions. The disclosed method utilizes curing with light irradiation, which is simple, convenient, easy to perform and apply and requires less energy demand. Furthermore, it enables easy upscaling.

Also advantageously, the composite materials may be of low viscosity. This advantageously results in a composite material which can be applied in an easy and controlled manner, leading to improved handling and uniform coatings of the electrolytes.

Furthermore, this ensures better interface quality and reduces the likelihood of defects of the electrolytes in the electrochromic devices. In addition, it may be easy to apply and handle a low viscosity electrolyte and thus the electrolyte is able to be applied directly on the electrode for in-situ polymerization of electrolyte in the electrochromic device. The in-situ method may be an effective approach to improve the processability and enhance electrolyte contact, while maintaining the dimension of the composite materials in the electrochromic devices, which in turn give excellent electrochromic performance.

Further advantageously, the polymer matrix may be formed by reaction of alkene with reactive groups which allows the polymer matrix to be formed via in-situ polymerization. This greatly enhances its processability and facilitates its translation into industrial settings, offering controllability over the manufacturing process.

According to another aspect of the present disclosure, there is provided a use of a composite material as an electrolyte sandwiched between two electrodes in an electrochromic device, the composite material comprising:

an ionic liquid A, wherein the ionic liquid A is 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (EMIMTFSI); and

a polymer matrix comprising a network of crosslinked poly(ionic liquid B), wherein the polymer matrix is formed by reaction of an ionic liquid B with a crosslinking agent, wherein the ionic liquid B is 1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl) imide (BVIMTFSI), and the crosslinking agent is poly(ethylene glycol) diacrylate (PEGDA)

Definitions

Unless otherwise defined herein, scientific and technical terms used in this application shall have the meanings that are commonly understood by those of ordinary skill in the art. Generally, nomenclature used in connection with, and techniques of, chemistry described herein, are those well-known and commonly used in the art.

Unless the context requires otherwise or specifically stated to the contrary, integers, steps, or elements of the invention recited herein as singular integers, steps or elements clearly encompass both singular and plural forms of the recited integers, steps or elements.

The following words and terms used herein shall have the meaning indicated:

As used herein, the term "alkyl group" includes within its meaning monovalent ("alkyl") and divalent ("alkylene") straight chain or branched chain saturated aliphatic groups having from 1 to 10 carbon atoms, e.g., 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 carbon atoms. For example, the term alkyl includes, but is not limited to, methyl, ethyl, 1-propyl, isopropyl, 1-butyl, 2-butyl, isobutyl, tert-butyl, amyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, pentyl, isopentyl, hexyl, 4-methylpentyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 2,2-dimethylbutyl, 3,3-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 1,2,2-trimethylpropyl, 1,1,2-trimethylpropyl, 2-ethylpentyl, 3-ethylpentyl, heptyl, 1-methylhexyl, 2,2-dimethylpentyl, 3,3-dimethylpentyl, 4,4-dimethylpentyl, 1,2-dimethylpentyl, 1,3-dimethylpentyl, 1,4-dimethylpentyl, 1,2,3-trimethylbutyl, 1,1,2-trimethylbutyl, 1,1,3-trimethylbutyl, 5-methylheptyl, 1-methylheptyl, octyl, nonyl, decyl, and the like.

The term "alkenyl group" includes within its meaning monovalent ("alkenyl") and divalent ("alkenylene") straight or branched chain unsaturated aliphatic hydrocarbon groups having from 2 to 10 carbon atoms, e.g., 2, 3, 4, 5, 6, 7, 8, 9, or 10 carbon atoms and having at least one double bond, of either E, Z, cis or trans stereochemistry where applicable, anywhere in the alkyl chain. Examples of alkenyl groups include but are not limited to ethenyl, vinyl, allyl, 1-methylvinyl, 1-propenyl, 2-propenyl, 2-methyl-1-propenyl, 2-methyl-1-propenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1,3-butadienyl, 1-pentenyl, 2-pentenyl, 3-pentenyl, 4-pentenyl, 1,3-pentadienyl, 2,4-pentadienyl, 1,4-pentadienyl, 3-methyl-2-butenyl, 1-hexenyl, 2-hexenyl, 3-hexenyl, 1,3-hexadienyl, 1,4-hexadienyl, 2-methylpentenyl, 1-heptenyl, 2-heptenyl, 3-heptenyl, 1-octenyl, 1-nonenyl, 1-decenyl, and the like.

The term "alkynyl group" as used herein includes within its meaning monovalent ("alkynyl") and divalent ("alkynylene") straight or branched chain unsaturated aliphatic hydrocarbon groups having from 2 to 10 carbon atoms and having at least one triple bond anywhere in the carbon chain. Examples of alkynyl

groups include but are not limited to ethynyl, 1-propynyl, 1-butyryl, 2-butyryl, 1-methyl-2-butyryl, 3-methyl-1-butyryl, 1-pentyryl, 1-hexyryl, methylpentyryl, 1-heptyryl, 2-heptyryl, 1-octyryl, 2-octyryl, 1-nonyl, 1-decyryl, and the like.

As used herein, the term “ionic liquid” refers to a salt in the liquid state. The term ‘ionic liquid’ may also refer to salts whose melting point is below a specific temperature, such as 100 °C.

As used herein, the term “poly(ionic liquid)s” or “PILs” refers to polymers composed of repeating units of ionic liquid moieties. The poly(ionic liquid) may be formed by polymerizing or copolymerizing monomers that contain ionic liquid functionalities. These monomers may have one or more ionic groups attached to a polymerizable backbone. The resulting polymer contains both covalent and ionic bonds within its structure.

As used herein, the term “network” refers to a three-dimensional structure formed by the chemical bonding or crosslinking of polymer chains. “Crosslinking” refers to the creation of covalent bonds between polymer chains, resulting in a three-dimensional interconnected network structure. In a network of crosslinked polymers, the polymer chains are chemically bonded together at various points, forming a continuous framework throughout the material. This network structure is different from linear polymers, where the polymer chains are not chemically interconnected.

The term “crosslinking agent” or “crosslinker” is to be interpreted broadly to include any chemicals added or used to form a network of crosslinking through the process of chemical crosslinking, physical linkage, ionic, and/or hydrogen bonding.

The word “substantially” does not exclude “completely” e.g., a composition which is “substantially free” from Y may be completely free from Y. Where necessary, the word “substantially” may be omitted from the definition of the invention.

Unless specified otherwise, the terms “comprising” and “comprise”, and grammatical variants thereof, are intended to represent “open” or “inclusive” language such that they include recited elements but also permit inclusion of additional, unrecited elements.

As used herein, the term “about”, in the context of concentrations of components of the formulations, typically means $\pm 5\%$ of the stated value, more typically $\pm 4\%$ of the stated value, more typically $\pm 3\%$ of the stated value, more typically, $\pm 2\%$ of the stated value, even more typically $\pm 1\%$ of the stated value, and even more typically $\pm 0.5\%$ of the stated value.

Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on

the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

Certain embodiments may also be described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the disclosure. This includes the generic description of the embodiments with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

Brief Description of Drawings

The accompanying drawings illustrate a disclosed embodiment and serves to explain the principles of the disclosed embodiment. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

Figure 1A

[Figure 1A] is a schematic illustration showing a precursor mixture of Composite Material A (CM A) of the present invention with its respective time-dependent Fourier-transform infrared (FTIR) spectra at 1850-1600 and 1000-800 cm^{-1} (at time = 0, 10, 20, 30, 40, and 50 seconds).

Figure 1B

[Figure 1B] is a schematic illustration showing a precursor mixture of Composite Material (CM B) of the present invention with its respective time-dependent Fourier-transform infrared (FTIR) spectra at 1850-1600 and 1000-800 cm^{-1} (at time = 0, 10, 20, 30, 40, and 50 seconds).

Figure 2

[Figure 2] shows ^1H Nuclear Magnetic Resonance (NMR) spectra of (a) 1-butyl-3-vinylimidazolium bromide (BVIMBr); and (b) 1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide (BVIMTFSI) in deuterated chloroform (CDCl_3).

Figure 3

[Figure 3] is a schematic illustration showing a mechanism of (a) photoinitiation; and (b) chain-mode radical photopolymerization.

Figure 4

[Figure 4] is a graphical plot of ionic conductivity ($\log \sigma$) with respect to loading of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIMTFSI) where it shows the optimization of conductivities of cured composite materials based on fraction of EMIMTFSI.

Figure 5

[Figure 5] shows scanning electron microscope (SEM) images of (a) composite material without addition of mobile phase (ionic liquid A) (hereon referred to as "Bare CM"), (b) CM A, and (c) CM B.

Figure 6A

[Figure 6A] shows an optical image of cured CM A (above) and CM B (below) with 1 mm thickness.

Figure 6B

[Figure 6B] shows a graphical plot of spectral transmittance of wavelength 250-1250nm of EMIMTFSI, CM A and CM B of 1 mm thickness/pathlength.

Figure 7A

[Figure 7A] shows a graphical plot of thermogravimetric analysis (TGA) of weight % against temperature (of EMIMTFSI, CM A and CM B).

Figure 7B

[Figure 7B] shows a graphical plot of differential scanning calorimetry (DSC) of heat flow against temperature of EMIMTFSI, CM A and CM B.

Figure 7C

[Figure 7C] shows a graphical plot of linear sweep voltammetry (LSV) of current density against potential of EMIMTFSI, CM A and CM B.

Figure 7D

[Figure 7D] shows a graphical plot of Arrhenius plot of ionic conductivity as a function of reciprocal temperature of CM A and CM B.

Figure 8

[Figure 8] is a graphical plot showing the thermogravimetric analysis (TGA) of EMIMTFSI, Bare CM and poly(ethylene glycol) diacrylate (PEGDA) 700.

Figure 9A

[Figure 9A] shows a scanning electron microscope (SEM) image of titanium dioxide nanoparticles coated (TiO₂ NP coated) fluorine doped tin oxide (FTO) electrode.

Figure 9B

[Figure 9B] shows a graphical plot of spectral transmittance of titanium dioxide nanoparticles coated (TiO₂ NP coated) fluorine doped tin oxide (FTO) electrode versus that of a fluorine doped tin oxide (FTO) electrode.

Figure 10

[Figure 10] is a schematic illustration showing a fabrication procedure of an electrochromic device with composite materials of the present invention via a combination of self-wetting and in-situ polymerization approach.

Figure 11A

[Figure 11A] is an optical image showing surface tension measurement of CM A of the present invention via the pendant drop method using a 20-gauge needle, where density of CM A is 1.392 g/cm³.

Figure 11B

[Figure 11B] is an optical image showing surface tension measurement of CM B of the present invention via the pendant drop method using a 20-gauge needle, where density of CM B is 1.348 g/cm³.

Figure 12

[Figure 12] shows cross-sectional images of an electrolyte layer of CM A of the present invention with 5, 10, 15 and 20 mL/cm² electrolyte.

Figure 13

[Figure 13] is an optical image of an iron-centered coordination polymer (FeCP) device with electrolyte comprising CM A which changes from purple (left) to pale yellow (right) upon oxidation.

Figure 14A

[Figure 14A] shows a graphical plot of cyclic voltammograms of FeCP electrochromic device comprising CM A at different scan rates (5 mV/s, 10mV/s, 20 mV/s, 50 mV/s, 100 mV/s, and 200mV/s).

Figure 14B

[Figure 14B] shows a graphical plot of spectral transmittance of FeCP device comprising CM A recorded at +1.0 V (bleached) and +2.3 V (coloured).

Figure 14C

[Figure 14C] shows a graphical plot of response times of a FeCP device comprising CM A for coloration (t_c) and bleaching (t_b) at 572 nm between potential of +1.0 V and +2.5 V at 10 s intervals.

Figure 14D

[Figure 14D] shows a graphical plot of changes in transmittance of a FeCP device comprising CM A at 572 nm recorded by applying alternating potential of +2.4 V and 1.0 V (with 10s interval) over 3000 cycles.

Figure 15

[Figure 15] shows a schematic illustration (left) and a cyclic voltammogram (right) of a FeCP device comprising CM A without TiO_2 counter electrode, where the oxidative and reductive couples are far apart which leads to higher operating potential range.

Figure 16

[Figure 16] is an optical image of a P- WO_3 device (where P- WO_3 denotes an electrode with a thin layer of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) coated onto a tungsten oxide (WO_3) electrode) with electrolyte comprising CM B which changes from transparent (left) to deep blue (right) upon reduction.

Figure 17A

[Figure 17A] shows a graphical plot of cyclic voltammograms of P- WO_3 electrochromic device comprising CM B at different scan rates (5 mV/s, 10mV/s, 20 mV/s, 50 mV/s, 100 mV/s, and 200mV/s).

Figure 17B

[Figure 17B] shows a graphical plot of spectral transmittance of P- WO_3 device comprising CM B recorded at +1.5 V (bleached) and -2.0 V (coloured).

Figure 17C

[Figure 17C] shows a graphical plot of response times of P-WO₃ device (a P-WO₃ device with electrolyte comprising CM B) for coloration (t_c) and bleaching (t_b) at 660 nm between potential of -2.0 V and +1.5 V at 15 s and 30 s intervals.

Figure 17D

[Figure 17D] shows a graphical plot of changes in transmittance of P-WO₃ device comprising CM B at 660 nm recorded by applying alternating potential of -2.0 V and +1.5 V at 15 s and 30 s intervals over 5000 cycles.

Figure 18

[Figure 18] shows a schematic illustration (left) and a cyclic voltammogram (right) of a P-WO₃ device comprising CM B without TiO₂ counter electrode, where the oxidative and reductive couples are far apart which leads to higher operating potential range.

Figure 19A

[Figure 19A] shows a graphical current-time plot of the P-WO₃ device comprising CM B at a temperature of -20, 20 and 100 °C.

Figure 19B

[Figure 19B] shows a graphical plot of the corresponding amount of charge derived by integrating the area of the P-WO₃ device comprising CM B at -20 °C, 20 °C and 100 °C as shown in Figure 19A.

Figure 19C

[Figure 19C] shows a graphical plot of transmittance of the P-WO₃ device comprising CM B under bleached and coloured states at -20 °C, 20 °C and 100 °C.

Figure 19D

[Figure 19D] shows a graphical plot of the corresponding optical contrast at 660 nm of the P-WO₃ device comprising CM B under bleached and coloured states at -20 °C, 20 °C and 100 °C as shown in Figure 19C.

Figure 20

[Figure 20] shows optical images of a flexible electrochromic eye protector device in (a) side view and (b) top view of a curved electrochromic device (ECD) based on ultra-thin ITO glass switching between coloured (-2.0 V) and bleached (+1.5 V) states.

Figure 21A

[Figure 21A] shows a schematic illustration of the reflective electrochromic display based on Copper-Nickel (Cu-Ni) conductive textiles.

Figure 21B

[Figure 21B] shows photographs of the reflective electrochromic display (when switched on and off) upon colour changing process in twisted form.

Figure 22A

[Figure 22A] shows a schematic illustration of a transmissive electrochromic display based on an indium-doped tin oxide (ITO) polyethylene terephthalate (PET) (ITO-PET) substrate.

Figure 22B

[Figure 22B] shows actual photographs of transmissive electrochromic displays colour switched (when switched on and off) at -20 °C (top) and 100 °C (bottom) upon bending.

Figure 23

[Figure 23] is a graphical plot showing contrast retention at 660 nm of a P-WO₃/ITO/PET device comprising CM B over 500 bending and flattening cycles.

Figure 24A

[Figure 24A] shows an illustration of the polymer matrix of composite material CM A of the present invention comprising a network of crosslinked poly(ionic liquid B).

Figure 24B

[Figure 24B] shows an illustration of the polymer matrix of composite material CM B of the present invention comprising a network of crosslinked poly(ionic liquid B).

Detailed Description of Drawings

As shown in Figures 24A and 24B, ionic liquid B undergoes polymerization with a crosslinking agent to form poly(ionic liquid B) which forms the polymer matrix. The polymerization may occur via photopolymerization. During polymerization, vinyl groups present in ionic liquid B may react with acrylate groups present in the crosslinking agent to form poly(ionic liquid B) that is bonded, crosslinked or interconnected at one or several points along the polymer chain to form a network of crosslinked poly(ionic liquid B).

Figure 24A shows a method of preparing CM A of the present invention. Ionic liquid B (BVIMTFSI) undergoes polymerization with PEGDA to form poly(BVIMTFSI) which forms the polymer matrix. The polymerization may occur via photopolymerization at 395 nm. During polymerization, vinyl groups present in BVIMTFSI react with acrylate groups present in PEGDA to form poly(BVIMTFSI) that is bonded, crosslinked or interconnected at one or several points along the polymer chain to form a network of crosslinked poly(BVIMTFSI).

Figure 24B shows a method of preparing CM B of the present invention. Ionic liquid B (BVIMTFSI) and lithium methacrylate trifluoroborate complex solution (with propylene carbonate) undergo polymerization with PEGDA to form a polymer matrix incorporated with Li^+ . The polymerization may occur via photopolymerization at 395 nm. During polymerization, reaction occurs between the vinyl groups present in BVIMTFSI, vinyl groups in lithium methacrylate trifluoroborate complex, and acrylate groups in PEGDA to form a polymer matrix that is bonded, crosslinked or interconnected at one or several points along the polymer chain with Li^+ incorporated in the polymer matrix.

Detailed Description of Embodiments

The following detailed description is merely exemplary in nature and is not intended to limit the invention or the application and uses of the invention. Furthermore, there is no intention to be bound by any theory presented in the preceding background of the invention or the following detailed description. It is the intent of the present invention to present a composite material and/or an electrochromic device that overcomes, or at least ameliorates, one or more of the disadvantages described earlier in the background of the disclosure.

Ionogels, which are composite materials consisting of an ionic liquid immobilized by an inorganic or a polymer matrix, are interesting alternatives to common liquid or gel electrolytes owing to their remarkable thermal and chemical stability, non-volatility, and good conductivity in solid state.

These composite materials are useful as electrolytes in electrochromic devices (ECDs). The electrolyte in an ECD is indispensable as it hosts essential ions for electrochromic reaction and balances residual charges, which influence the switching performance. In addition, the use of ionic liquids or ionic liquid additives in these composite materials as electrolytes could reduce electrochromic driving potential and improve their kinetics, hence reducing degradation (such as materials, electrolyte, or ion-trapping-induced degradation), leading to an enhancement of electrochromic performance. Enabled by these properties, these composite materials may be used in a variety of flexible electronics such as actuators, transistors, sensors, nanogenerators, and energy storage devices.

These composite materials when used as electrolytes, display outstanding advantages in electrochromic applications, but conventional hosting polymers could lead to poor compatibility, causing seepages upon mechanical deformation and macroscopic phase separation at extreme temperatures.

Poly(ionic liquid)s or PILs, which are chemically similar to ionic liquids, are potential substitutes. However, the preparation of PILs has not been straightforward alongside a lack of controllability in polymer dimensions. Such pre-made polymers when used as electrolytes are difficult to apply and could cause poor penetration of ionic species into the electrochromic layer.

To address the issue and limitations of pre-made polymer electrolytes, inert polymer matrices can be employed solely to facilitate the encapsulation of ionic liquids. However, poor compatibility between ionic liquid (mobile phase) and its corresponding polymer networks can easily lead to seepages upon mechanical deformation and macroscopic phase separation at extreme temperatures, which would undermine the transparency, electrochemical behaviours, and practicality of the composite materials. In addition, composite materials that are prepared with hydrophilic polymer matrices are often causing unstable performances in a humid environment.

To address the challenges discussed above and also in the background earlier, the inventors present a composite material and/or an electrochromic device as discussed below.

With the above considerations, poly(ionic liquid)s (PILs) in which the polymer backbone/ polymer matrix and ionic liquid (mobile phase) can be compatibilized, are potential substitutes for these conventional host polymer matrices.

Composite Material

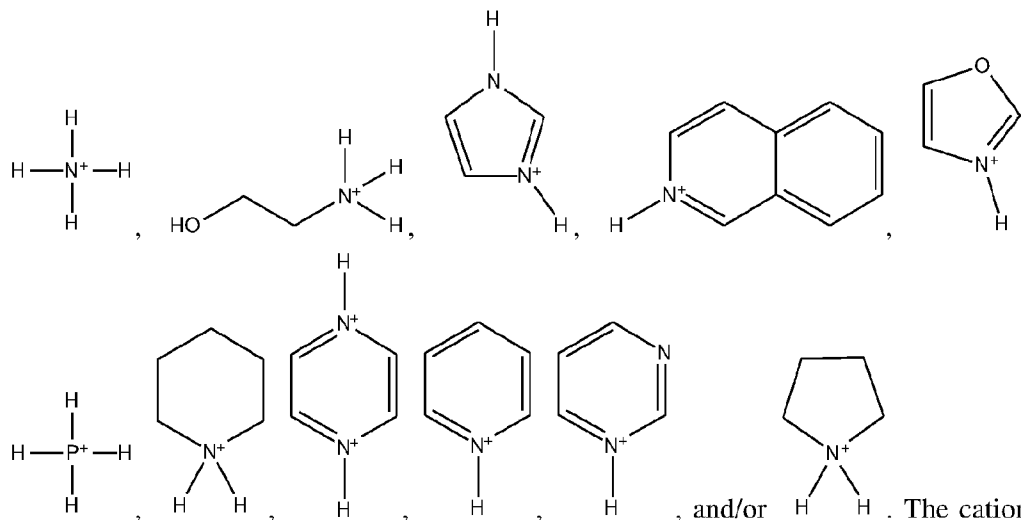
The present invention relates to a composite material comprising: an ionic liquid A; and a polymer matrix comprising a network of crosslinked poly(ionic liquid B).

Ionic liquid A and/or ionic liquid B may be salts in the liquid state whose melting point may be below a temperature of 100 °C. The present invention relates to a composite material wherein ionic liquid A and ionic liquid B may be the same. The present invention also relates to a composite material wherein ionic liquid A and ionic liquid B may be different.

Ionic liquid A and/or ionic liquid B may each comprise a cation comprising ammonium, cholinium, imidazolium, isoquinolinium, oxazolium, phosphonium, piperidinium, pyrazinium, pyridinium, pyrimidinium, and pyrrolidinium, or any

combinations thereof. The cation may be unsubstituted or substituted with groups selected from alkyl, alkenyl or alkynyl groups. For example, ionic liquid A and/or ionic liquid B may each comprise an imidazolium cation substituted with alkyl and/or alkenyl groups. Ionic liquid A and/or ionic liquid B may comprise an imidazolium cation substituted with a C₂ alkenyl and a C₄ alkyl, or may comprise an imidazolium cation substituted with a C₁ alkyl and a C₂ alkyl.

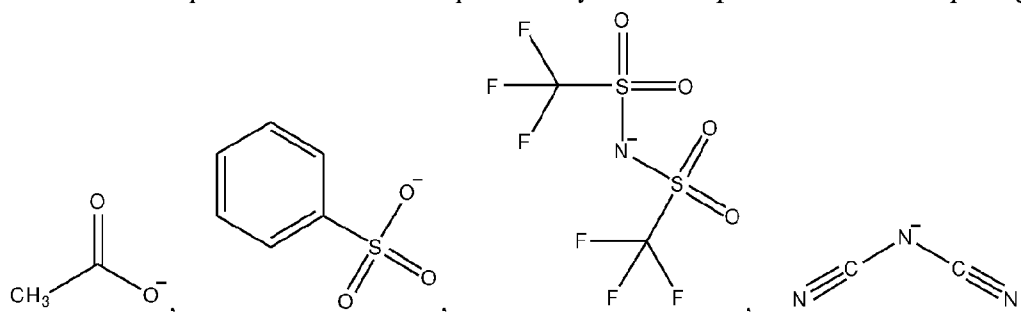
Ionic liquid A and/or ionic liquid B may each comprise a cation comprising

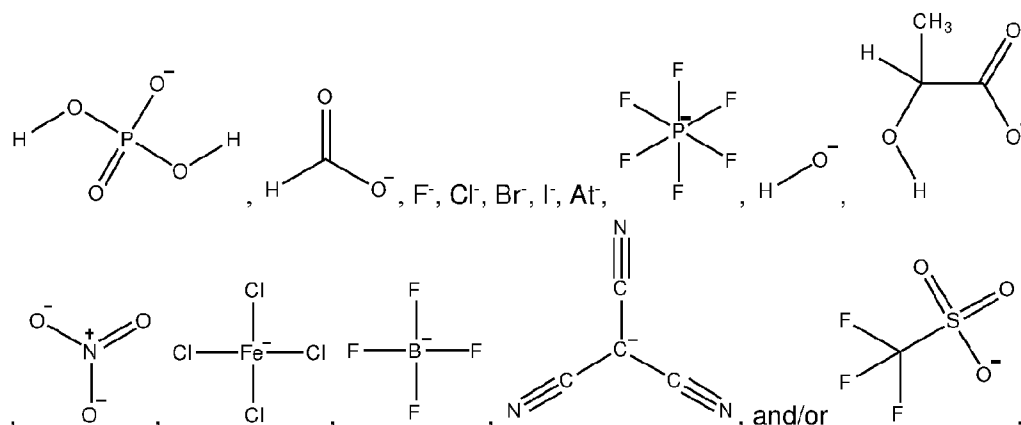


The cation may be unsubstituted or substituted with groups selected from alkyl, alkenyl or alkynyl groups. For example, ionic liquid A and/or ionic liquid B may each comprise an imidazolium cation substituted at least once with alkyl and/or alkenyl groups. Ionic liquid A and/or ionic liquid B may comprise an imidazolium cation substituted with a C₂ alkenyl and a C₄ alkyl, or may comprise an imidazolium cation substituted with a C₁ alkyl and a C₂ alkyl.

Ionic liquid A and/or ionic liquid B may each comprise an anion comprising acetate, benzenesulphonate, bistriflimide, dicyanamide, dihydrogenphosphate, formate, halide (fluoride, chloride, bromide, iodide, astatide), hexafluorophosphate, hydroxide, lactate, nitrate, tetrachloroferrate, tetrafluoroborate, tricyanomethanide, and triflate, or any combinations thereof

Ionic liquid A and/or ionic liquid B may each comprise an anion comprising





Ionic liquid A may comprise a cation substituted at least once with C_1 to C_{10} alkyl, with C_2 to C_{10} alkyl, C_3 to C_{10} alkyl, C_4 to C_{10} alkyl, C_5 to C_{10} alkyl, C_6 to C_{10} alkyl, C_7 to C_{10} alkyl, C_8 to C_{10} alkyl, C_9 to C_{10} alkyl, C_1 to C_9 alkyl, C_1 to C_8 alkyl, C_1 to C_7 alkyl, C_1 to C_6 alkyl, C_1 to C_5 alkyl, C_1 to C_4 alkyl, C_1 to C_3 alkyl, C_1 to C_2 alkyl, C_1 alkyl, C_2 alkyl, C_3 alkyl, C_4 alkyl, C_5 alkyl, C_6 alkyl, C_7 alkyl, C_8 alkyl, C_9 alkyl, C_{10} alkyl, or any combinations thereof.

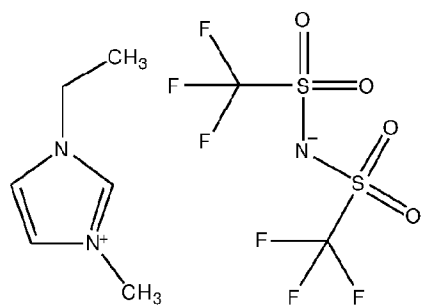
Ionic liquid B may comprise a cation substituted at least once with C_2 to C_{10} alkene, with C_3 to C_{10} alkene, with C_4 to C_{10} alkene, with C_5 to C_{10} alkene, with C_6 to C_{10} alkene, with C_7 to C_{10} alkene, with C_8 to C_{10} alkene, with C_9 to C_{10} alkene, with C_2 to C_9 alkene, with C_2 to C_8 alkene, with C_2 to C_7 alkene, with C_2 to C_6 alkene, with C_2 to C_5 alkene, with C_2 to C_4 alkene, with C_2 to C_3 alkene, with C_2 alkene, with C_3 alkene, with C_4 alkene, with C_5 alkene, with C_6 alkene, with C_7 alkene, with C_8 alkene, with C_9 alkene, with C_{10} alkene, or any combinations thereof.

Ionic liquid A may be selected from the group consisting of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (EMIMTFSI), 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF₄), 1-ethyl-3-methylimidazolium hexafluorophosphate (EMIM-PF₆), 1-ethyl-3-methylimidazolium acetate (EMIM-Ac), 1-ethyl-3-methylimidazolium dicyanamide (EMIM-DCA), butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIMTFSI), 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM-BF₄), 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF₆), 1-butyl-3-methylimidazolium acetate (BMIM-Ac), 1-Butyl-3-methylimidazolium dicyanamide (BMIM-DCA), or any combinations thereof.

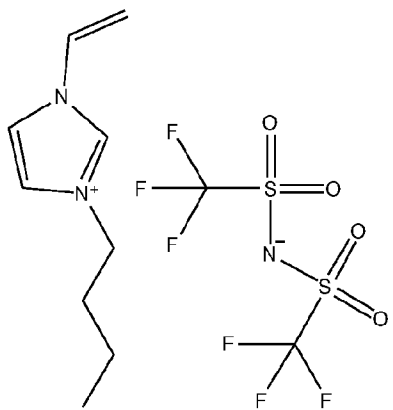
Ionic liquid B may be selected from the group consisting of 1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl) imide (BVIMTFSI), 1-ethyl-3-vinylimidazolium bis(trifluoromethanesulfonyl) imide (EVIMTFSI), 1-ethyl-3-vinylimidazolium tetrafluoroborate (EVIM-BF₄), 1-ethyl-3-vinylimidazolium hexafluorophosphate (EVIM-PF₆), 1-ethyl-3-vinylimidazolium acetate (EVIM-Ac), 1-ethyl-3-vinylimidazolium dicyanamide (EVIM-DCA), 1-butyl-3-vinylimidazolium tetrafluoroborate (BVIM-BF₄), 1-butyl-3-vinylimidazolium hexafluorophosphate

(BVIM-PF₆), 1-butyl-3-vinylimidazolium acetate (BVIM-Ac), 1-butyl-3-vinylimidazolium dicyanamide (BVIM-DCA), 1-pentyl-3-vinylimidazolium bis(trifluoromethanesulfonyl) imide (PVIMTFSI), 1-pentyl-3-vinylimidazolium tetrafluoroborate (PVIM-BF₄), 1-pentyl-3-vinylimidazolium hexafluorophosphate (PVIM-PF₆), 1-pentyl-3-vinylimidazolium acetate (PVIM-Ac), 1-pentyl-3-vinylimidazolium dicyanamide (PVIM-DCA), 1-hexyl-3-vinylimidazolium bis(trifluoromethanesulfonyl) imide (HVIMTFSI), 1-hexyl-3-vinylimidazolium tetrafluoroborate (HVIM-BF₄), 1-hexyl-3-vinylimidazolium hexafluorophosphate (PVIM-PF₆), 1-hexyl-3-vinylimidazolium acetate (HVIM-Ac), 1-hexyl-3-vinylimidazolium dicyanamide (HVIM-DCA), or any combinations thereof.

Ionic liquid A may be 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (EMIMTFSI):



Ionic liquid B may be 1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl) imide (BVIMTFSI):



The polymer matrix in the composite material may comprise a network of crosslinked poly(ionic liquid B) as depicted in Figures 24A and 24B. As shown in Figures 24A and 24B, the polymer matrix is a three-dimensional structure interconnected network structure where the polymer chains are chemically bonded together at various points, forming a continuous framework throughout the material.

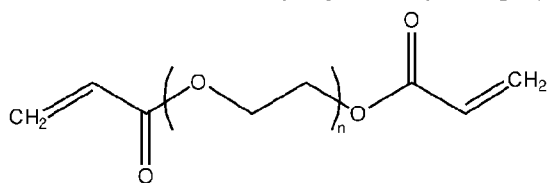
To form the polymer matrix, ionic liquid B may be polymerized with a crosslinking agent. The polymerization may occur via photopolymerization. During polymerization, vinyl groups on ionic liquid B may react with acrylate groups on the crosslinking agent to form poly(ionic liquid B) that is bonded, crosslinked or interconnected at one or several points along the polymer chain to form a network of crosslinked poly(ionic liquid B). Ionic liquid A may be dispersed throughout the polymer matrix to form the composite material of the present invention. Ionic liquid A may have interactions with the polymer matrix predominantly in the form of interactions such as electrostatic interactions, and hydrogen bonding interactions. These electrostatic interactions may stabilize and facilitate charge transfer of ions in response to the applied electric field which make the electrolytes of the present invention excellent material for electrochromic devices.

Additionally, the electrolytes of the present invention may comprise a homogenous polymer matrix that does not phase separate when it undergoes changes in temperature. The homogenous polymer matrix advantageously improves the structural integrity of the composite material by having a consistent distribution of components within the polymer matrix helps distribute stress and load evenly across the polymer matrix. This reduces the likelihood of localized weak points or areas prone to failure. Furthermore, a homogenized matrix ensures a uniform performance across the composite material.

The use of poly(ionic liquid) as the polymer matrix not only facilitates the incorporation of ionic liquids due to chemical resemblance or similarity, but they could also enrich the properties of the composite materials/ionogels with different modifications. For example, aqueous solubility of poly(ionic liquid) can be easily controlled through simple counterions exchange. By replacing halides counterions with bis(trifluoromethane)sulfonimide anion (TFSI⁻) or hexafluorophosphate anion (PF₆⁻), the poly(ionic liquid) blocks could turn from hydrophilic to hydrophobic, inducing aggregates formation and changes moisture sensitivity of the polymer.

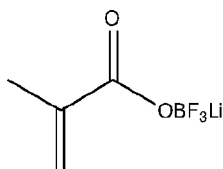
The crosslinking agent may comprise vinyl or acrylate groups. Polymer matrix may be formed by a reaction of the alkene of ionic liquid B with the acrylate group of the crosslinking agent. The crosslinking agent may be poly(ethylene glycol) diacrylate (PEGDA).

The crosslinking agent may be poly(ethylene glycol) diacrylate (PEGDA):



, wherein n is an integer selected from 1 to 25, or n is 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, or 25.

The present invention also relates to a composite material, wherein the composite material further comprises a metal borate complex. The metal borate complex may contain a metal selected from the group consisting of sodium, lithium and combinations thereof. The metal borate complex may comprise one or more vinyl groups. The metal borate complex may comprise one or more acrylates. The metal borate complex may be a metal methacrylate trifluoroborate complex. The metal borate complex may be lithium



methacrylate trifluoroborate:

In an embodiment of the present invention, the composite material may further comprise a metal borate complex. The metal borate complex may be added in combination with a plasticizer. Vinyl groups on the metal borate complex, vinyl groups on the ionic liquid B, and acrylate groups on the crosslinking agent may react with each other and undergo polymerization to form the polymer matrix. The polymerization may occur via photopolymerization. This network is illustrated in Figure 24B.

The plasticizer may be ethylene carbonate, propylene carbonate (PC), dicarboxylic/tricarboxylic ester-based plasticizers, phthalate-based plasticizers (such as bis(2-ethylhexyl) phthalate (DEHP), diisononyl phthalate (DINP), bis(n-butyl)phthalate (DnBP, DBP), butyl benzyl phthalate (BBzP), diisodecyl phthalate (DIDP), di-n-octyl phthalate (DOP or DnOP), diisooctyl phthalate (DIOP), diethyl phthalate (DEP), diisobutyl phthalate (DIBP), and di-n-hexyl phthalate), trimellitates (such as trimethyl trimellitate (TMTM), tri-(2-ethylhexyl) trimellitate (TEHTM-MG), tri-(n-octyl,n-decyl) trimellitate (ATM), tri-(heptyl,nonyl) trimellitate (LTM), and n-octyl trimellitate (OTM)), adipate-based plasticizers (such as bis(2-ethylhexyl)adipate (DEHA), dimethyl adipate (DMAD), monomethyl adipate (MMAD), and dioctyl adipate (DOA)), sebacate-based plasticiser (such as dibutyl sebacate (DBS)), maleates (such as dibutyl maleate (DBM), and diisobutyl maleate (DIBM)), benzoates, epoxidized vegetable oils, sulfonamides (such as n-ethyl toluene sulfonamide (o/p ETSA), ortho and para isomers, n-(2-hydroxypropyl) benzene sulfonamide (HP BSA), n-(n-butyl) benzene sulfonamide (BBSA-NBBS)), organophosphates, tricresyl phosphate (TCP), tributyl phosphate (TBP), glycols/polyethers, triethylene glycol dihexanoate (3G6, 3GH), tetraethylene glycol diheptanoate (4G7), acetylated monoglycerides, alkyl citrates, triethyl citrate (TEC), acetyl triethyl citrate (ATEC), tributyl citrate (TBC), acetyl tributyl citrate (ATBC), trioctyl citrate (TOC), acetyl trioctyl citrate (ATOC), trihexyl citrate (THC), acetyl trihexyl citrate (ATHC), butyryl trihexyl citrate (BTHC, trihexyl o-butyryl citrate), or trimethyl citrate (TMC).

In such embodiments, the polymer matrix may comprise a metal-ion-containing polymer backbone (for example, an Li-ion-containing polymer backbone). The composite material may further comprise a plasticizer (for example, propylene carbonate). The

metal-ion-containing polymer backbone serves as a metal-ion source and together with the plasticizer, may facilitate metal-ion transportation.

The metal in a metal borate complex has a lower ionic interaction as compared to the metal in a metal complex, which allows the metal ions to dissociate more easily. For example, the lithium ion in lithium methacrylate trifluoroborate has a lower ionic interaction when compared to the lithium ion in lithium methacrylate, which is directly bound to the -O- (i.e., Li-O-). In such metal complexes, due to the high ionic interaction between the metal ion and the complex, the metal ion may only dissociate in a polar protic solvent, which is not ideal for electrochemical applications as protic solvent has poor electrochemical stability. Hence, by using a metal borate complex, dissociation of metal ions becomes possible within the polymer matrix and plasticizer without the use of polar protic solvent which improves electrochemical performance. Additionally, such composite materials comprising metal borate complex are also stable.

In one embodiment, the composite material may comprise the following, wherein the ionic liquid A is 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (EMIMTFSI); the ionic liquid B is 1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl) imide (BVIMTFSI); and the crosslinking agent is poly(ethylene glycol) diacrylate (PEGDA).

In another embodiment, the composite material may comprise the following, wherein the ionic liquid A is 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (EMIMTFSI); the ionic liquid B is 1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl) imide (BVIMTFSI); the crosslinking agent is poly(ethylene glycol) diacrylate (PEGDA); and the metal borate complex is lithium methacrylate trifluoroborate complex in propylene carbonate.

The composite material may be an ionogel.

The composite material may exhibit a transmittance of about 90% to about 98% in the visible and part of near-infrared region (380 nm to 1250 nm). The composite material may exhibit a transmittance of about 90.2% to about 98%, or of about 90.4% to about 98%, or of about 90.6% to about 98%, or of about 90.8% to about 98%, or of about 91% to about 98%, or of about 91.2% to about 98%, or of about 91.4% to about 98%, or of about 91.6% to about 98%, or of about 91.8% to about 98%, or of about 92% to about 98%, or of about 92.2% to about 98%, or of about 92.4% to about 98%, or of about 92.6% to about 98%, or of about 92.8% to about 98%, or of about 93% to about 98%, or of about 93.2% to about 98%, or of about 93.4% to about 98%, or of about 93.6% to about 98%, or of about 93.8% to about 98%, or of about 94% to about 98%, or of about 94.2% to about 98%, or of about 94.4% to about 98%, or of about 94.6% to about 98%, or of about 94.8% to about 98%, or of about 95% to about 98%, or of about 95.2% to about 98%, or of about 95.4% to about 98%, or of about 95.6% to about 98%, or of about 95.8% to about 98%, or of about 96% to about 98%, or of about 96.2% to about 98%, or of about 96.4% to about 98%, or of about 96.6% to about 98%, or of about 96.8% to about 98%, or of

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The composite material may exhibit a transmittance of about 90% to about 98% at 1 mm thickness, or of about 90.2% to about 98%, or of about 90.4% to about 98%, or of about 90.6% to about 98%, or of about 90.8% to about 98%, or of about 91% to about 98%, or of about 91.2% to about 98%, or of about 91.4% to about 98%, or of about 91.6% to about 98%, or of about 91.8% to about 98%, or of about 92% to about 98%, or of about 92.2% to about 98%, or of about 92.4% to about 98%, or of about 92.6% to about 98%, or of about 92.8% to about 98%, or of about 93% to about 98%, or of about 93.2% to about 98%, or of about 93.4% to about 98%, or of about 93.6% to about 98%, or of about 93.8% to about 98%, or of about 94% to about 98%, or of about 94.2% to about 98%, or of about 94.4% to about 98%, or of about 94.6% to about 98%, or of about 94.8% to about 98%, or of about 95% to about 98%, or of about 95.2% to about 98%, or of about 95.4% to about 98%, or of about 95.6% to about 98%, or of about 95.8% to about 98%, or of about 96% to about 98%, or of about 96.2% to about 98%, or of about 96.4% to about 98%, or of about 96.6% to about 98%, or of about 96.8% to about 98%, or of about 97%

to about 98%, or of about 97.2% to about 98%, or of about 97.4% to about 98%, or of about 97.6% to about 98%, or of about 97.8% to about 98%, of about 90% to about 97.8%, of about 90% to about 97.6%, of about 90% to about 97.4%, of about 90% to about 97.2%, of about 90% to about 97%, of about 90% to about 96.8%, of about 90% to about 96.6%, of about 90% to about 96.4%, of about 90% to about 96.2%, of about 90% to about 96%, of about 90% to about 95.8%, of about 90% to about 95.6%, of about 90% to about 95.4%, of about 90% to about 95.2%, of about 90% to about 95%, of about 90% to about 94.8%, of about 90% to about 94.6%, of about 90% to about 94.4%, of about 90% to about 94.2%, of about 90% to about 94%, of about 90% to about 93.8%, of about 90% to about 93.6%, of about 90% to about 93.4%, of about 90% to about 93.2%, of about 90% to about 93%, of about 90% to about 92.8%, of about 90% to about 92.6%, of about 90% to about 92.4%, of about 90% to about 92.2%, of about 90% to about 92%, of about 90% to about 91.8%, of about 90% to about 91.6%, of about 90% to about 91.4%, of about 90% to about 91.2%, of about 90% to about 91%, of about 90% to about 90.8%, of about 90% to about 90.6%, of about 90% to about 90.4%, of about 90% to about 90.2%, about 90%, about 90.1%, about 90.2%, about 90.3%, about 90.4%, about 90.5%, about 90.6%, about 90.7%, about 90.8%, about 90.9%, about 91%, about 91.1%, about 91.2%, about 91.3%, about 91.4%, about 91.5%, about 91.6%, about 91.7%, about 91.8%, about 91.9%, about 92%, about 92.1%, about 92.2%, about 92.3%, about 92.4%, about 92.5%, about 92.6%, about 92.7%, about 92.8%, about 92.9%, about 93%, about 93.1%, about 93.2%, about 93.3%, about 93.4%, about 93.5%, about 93.6%, about 93.7%, about 93.8%, about 93.9%, about 94%, about 94.1%, about 94.2%, about 94.3%, about 94.4%, about 94.5%, about 94.6%, about 94.7%, about 94.8%, about 94.9%, about 95%, about 95.1%, about 95.2%, about 95.3%, about 95.4%, about 95.5%, about 95.6%, about 95.7%, about 95.8%, about 95.9%, about 96%, about 96.1%, about 96.2%, about 96.3%, about 96.4%, about 96.5%, about 96.6%, about 96.7%, about 96.8%, about 96.9%, about 97%, about 97.1%, about 97.2%, about 97.3%, about 97.4%, about 97.5%, about 97.6%, about 97.7%, about 97.8%, about 97.9%, about 98%, or any range or value therebetween, at 1 mm thickness.

Crosslink density of the composite materials in moles/gram have been calculated by determining the number of moles of crosslinker and dividing by mass of the composite material. Alternatively, crosslink density of the composite materials (mol/cm³) may also be determined by number of moles of crosslinker and dividing it by volume of the composite material. The calculated crosslink density may be about 0.02 to about 0.05 mol/g, about 0.021 to about 0.05 mol/g, about 0.022 to about 0.05 mol/g, about 0.023 to about 0.05 mol/g, about 0.024 to about 0.05 mol/g, about 0.025 to about 0.05 mol/g, about 0.026 to about 0.05 mol/g, about 0.027 to about 0.05 mol/g, about 0.028 to about 0.05 mol/g, about 0.029 to about 0.05 mol/g, about 0.03 to about 0.05 mol/g, about 0.031 to about 0.05 mol/g, about 0.032 to about 0.05 mol/g, about 0.033 to about 0.05 mol/g, about 0.034 to about 0.05 mol/g, about 0.035 to about 0.05 mol/g, about 0.036 to about 0.05 mol/g, about 0.037 to about 0.05 mol/g, about 0.038 to about 0.05 mol/g, about 0.039 to about 0.05 mol/g, about 0.04 to about 0.05 mol/g, about 0.041 to about 0.05 mol/g, about 0.042 to about 0.05 mol/g, about 0.043 to about 0.05 mol/g, about 0.044 to about 0.05

mol/g, about 0.045 to about 0.05 mol/g, about 0.046 to about 0.05 mol/g, about 0.047 to about 0.05 mol/g, about 0.048 to about 0.05 mol/g, about 0.049 to about 0.05 mol/g, about 0.02 to about 0.049 mol/g, about 0.02 to about 0.048 mol/g, about 0.02 to about 0.047 mol/g, about 0.02 to about 0.046 mol/g, about 0.02 to about 0.045 mol/g, about 0.02 to about 0.044 mol/g, about 0.02 to about 0.043 mol/g, about 0.02 to about 0.042 mol/g, about 0.02 to about 0.041 mol/g, about 0.02 to about 0.04 mol/g, about 0.02 to about 0.039 mol/g, about 0.02 to about 0.038 mol/g, about 0.02 to about 0.037 mol/g, about 0.02 to about 0.036 mol/g, about 0.02 to about 0.035 mol/g, about 0.02 to about 0.034 mol/g, about 0.02 to about 0.033 mol/g, about 0.02 to about 0.032 mol/g, about 0.02 to about 0.031 mol/g, about 0.02 to about 0.03 mol/g, about 0.02 to about 0.029 mol/g, about 0.02 to about 0.028 mol/g, about 0.02 to about 0.027 mol/g, about 0.02 to about 0.026 mol/g, about 0.02 to about 0.025 mol/g, about 0.02 to about 0.024 mol/g, about 0.02 to about 0.023 mol/g, about 0.02 to about 0.022 mol/g, about 0.02 to about 0.021 mol/g, about 0.02, about 0.021, about 0.022, about 0.023, about 0.024, about 0.025, about 0.026, about 0.027, about 0.028, about 0.029, about 0.03, about 0.031, about 0.032, about 0.033, about 0.034, about 0.035, about 0.036, about 0.037, about 0.038, about 0.039, about 0.04, about 0.041, about 0.044, about 0.043, about 0.044, about 0.045, about 0.046, about 0.047, about 0.048, about 0.049, about 0.05, or any range or value therebetween.

The crosslink density may also be about 0.035 mol/cm³ to about 0.06 mol/cm³, about 0.035 to about 0.059, about 0.035 to about 0.058, about 0.035 to about 0.057, about 0.035 to about 0.056, about 0.035 to about 0.055, about 0.035 to about 0.054, about 0.035 to about 0.053, about 0.035 to about 0.052, about 0.035 to about 0.051, about 0.035 to about 0.050, about 0.035 to about 0.049, about 0.035 to about 0.048, about 0.035 to about 0.047, about 0.035 to about 0.046, about 0.035 to about 0.045, about 0.035 to about 0.044, about 0.035 to about 0.043, about 0.035 to about 0.042, about 0.035 to about 0.041, about 0.035 to about 0.040, about 0.035 to about 0.039, about 0.035 to about 0.038, about 0.035 to about 0.037, about 0.035 to about 0.036, about 0.035, about 0.036, about 0.037, about 0.038, about 0.039, about 0.04, about 0.041, about 0.042, about 0.043, about 0.044, about 0.045, about 0.046, about 0.047, about 0.048, about 0.049, about 0.050, about 0.051, about 0.052, about 0.053, about 0.054, about 0.055, about 0.056, about 0.057, about 0.058, about 0.059, about 0.06 mol/cm³, or any range or value therebetween.

Method of Preparing Composite Material

In this disclosure, highly transparent and flexible composite materials may be prepared via rapid photopolymerization under ambient conditions.

The present invention relates to a method of preparing a composite material disclosed herein, comprising the steps of: (i) preparing a mixture of ionic liquid A, ionic liquid B, crosslinking agent, and a photoinitiator; (ii) curing the mixture with light irradiation, wherein the crosslinking agent reacts with ionic liquid B to form a polymer matrix comprising a network of crosslinked poly(ionic liquid B).

The method may further comprises adding a metal borate complex in step (i).

Step (ii) relates to curing the mixture with light irradiation. Upon irradiation, the crosslinking agent reacts with ionic liquid B to form a polymer matrix comprising a network of crosslinked poly(ionic liquid B). Through the irradiation, a network of crosslinked poly(ionic liquids) in the composite material is formed which serve as the stationary phase to anchor ionic liquid A (mobile phase) to form the composite material.

For step (ii), the irradiated light may be of a wavelength of about 300 nm to about 500 nm, about 305 nm to about 500 nm, about 310 nm to about 500 nm, about 315 nm to about 500 nm, about 320 nm to about 500 nm, about 325 nm to about 500 nm, about 330 nm to about 500 nm, about 335 nm to about 500 nm, about 340 nm to about 500 nm, about 345 nm to about 500 nm, about 350 nm to about 500 nm, about 355 nm to about 500 nm, about 360 nm to about 500 nm, about 365 nm to about 500 nm, about 370 nm to about 500 nm, about 375 nm to about 500 nm, about 380 nm to about 500 nm, about 385 nm to about 500 nm, about 390 nm to about 500 nm, about 395 nm to about 500 nm, about 400 nm to about 500 nm, about 405 nm to about 500 nm, about 410 nm to about 500 nm, about 415 nm to about 500 nm, about 420 nm to about 500 nm, about 425 nm to about 500 nm, about 430 nm to about 500 nm, about 435 nm to about 500 nm, about 440 nm to about 500 nm, about 445 nm to about 500 nm, about 450 nm to about 500 nm, about 455 nm to about 500 nm, about 460 nm to about 500 nm, about 465 nm to about 500 nm, about 470 nm to about 500 nm, about 475 nm to about 500 nm, about 480 nm to about 500 nm, about 485 nm to about 500 nm, about 490 nm to about 500 nm, about 495 nm to about 500 nm, about 300 nm to about 495 nm, about 300 nm to about 490 nm, about 300 nm to about 485 nm, about 300 nm to about 480 nm, about 300 nm to about 475 nm, about 300 nm to about 470 nm, about 300 nm to about 465 nm, about 300 nm to about 460 nm, about 300 nm to about 455 nm, about 300 nm to about 450 nm, about 300 nm to about 445 nm, about 300 nm to about 440 nm, about 300 nm to about 435 nm, about 300 nm to about 430 nm, about 300 nm to about 425 nm, about 300 nm to about 420 nm, about 300 nm to about 415 nm, about 300 nm to about 410 nm, about 300 nm to about 405 nm, about 300 nm to about 400 nm, about 300 nm to about 395 nm, about 300 nm to about 390 nm, about 300 nm to about 385 nm, about 300 nm to about 380 nm, about 300 nm to about 375 nm, about 300 nm to about 370 nm, about 300 nm to about 365 nm, about 300 nm to about 360 nm, about 300 nm to about 355 nm, about 300 nm to about 350 nm, about 300 nm to about 345 nm, about 300 nm to about 340 nm, about 300 nm to about 335 nm, about 300 nm to about 330 nm, about 300 nm to about 325 nm, about 300 nm to about 320 nm, about 300 nm to about 315 nm, about 300 nm to about 310 nm, about 300 nm to about 305 nm, about 300 nm, about 301 nm, about 302 nm, about 303 nm, about 304 nm, about 305 nm, about 306 nm, about 307 nm, about 308 nm, about 309 nm, about 310 nm, about 311 nm, about 312 nm, about 313 nm, about 314 nm, about 315 nm, about 316 nm, about 317 nm, about 318 nm, about 319 nm, about 320 nm, about 321 nm, about 322 nm, about 323 nm, about 324 nm, about 325 nm, about 326 nm, about 327 nm, about 328 nm, about 329 nm, about 330 nm, about 331 nm, about 332 nm,

about 333 nm, about 334 nm, about 335 nm, about 336 nm, about 337 nm, about 338 nm, about 339 nm, about 340 nm, about 341 nm, about 342 nm, about 343 nm, about 344 nm, about 345 nm, about 346 nm, about 347 nm, about 348 nm, about 349 nm, about 350 nm, about 351 nm, about 352 nm, about 353 nm, about 354 nm, about 355 nm, about 356 nm, about 357 nm, about 358 nm, about 359 nm, about 360 nm, about 361 nm, about 362 nm, about 363 nm, about 364 nm, about 365 nm, about 366 nm, about 367 nm, about 368 nm, about 369 nm, about 370 nm, about 371 nm, about 372 nm, about 373 nm, about 374 nm, about 375 nm, about 376 nm, about 377 nm, about 378 nm, about 379 nm, about 380 nm, about 381 nm, about 382 nm, about 383 nm, about 384 nm, about 385 nm, about 386 nm, about 387 nm, about 388 nm, about 389 nm, about 390 nm, about 391 nm, about 392 nm, about 393 nm, about 394 nm, about 395 nm, about 396 nm, about 397 nm, about 398 nm, about 399 nm, about 400 nm, about 401 nm, about 402 nm, about 403 nm, about 404 nm, about 405 nm, about 406 nm, about 407 nm, about 408 nm, about 409 nm, about 410 nm, about 411 nm, about 412 nm, about 413 nm, about 414 nm, about 415 nm, about 416 nm, about 417 nm, about 418 nm, about 419 nm, about 420 nm, about 421 nm, about 422 nm, about 423 nm, about 424 nm, about 425 nm, about 426 nm, about 427 nm, about 428 nm, about 429 nm, about 430 nm, about 431 nm, about 432 nm, about 433 nm, about 434 nm, about 435 nm, about 436 nm, about 437 nm, about 438 nm, about 439 nm, about 440 nm, about 441 nm, about 442 nm, about 443 nm, about 444 nm, about 445 nm, about 446 nm, about 447 nm, about 448 nm, about 449 nm, about 450 nm, about 451 nm, about 452 nm, about 453 nm, about 454 nm, about 455 nm, about 456 nm, about 457 nm, about 458 nm, about 459 nm, about 460 nm, about 461 nm, about 462 nm, about 463 nm, about 464 nm, about 465 nm, about 466 nm, about 467 nm, about 468 nm, about 469 nm, about 470 nm, about 471 nm, about 472 nm, about 473 nm, about 474 nm, about 475 nm, about 476 nm, about 477 nm, about 478 nm, about 479 nm, about 480 nm, about 481 nm, about 482 nm, about 483 nm, about 484 nm, about 485 nm, about 486 nm, about 487 nm, about 488 nm, about 489 nm, about 490 nm, about 491 nm, about 492 nm, about 493 nm, about 494 nm, about 495 nm, about 496 nm, about 497 nm, about 498 nm, about 499 nm, about 500 nm, or any range or value therebetween.

Step (ii) may be performed at an irradiance of about 1.4 mW/cm² to about 4.2 mW/cm², about 1.4 mW/cm² to about 4.1 mW/cm², about 1.4 mW/cm² to about 4.0 mW/cm², about 1.4 mW/cm² to about 3.9 mW/cm², about 1.4 mW/cm² to about 3.8 mW/cm², about 1.4 mW/cm² to about 3.7 mW/cm², about 1.4 mW/cm² to about 3.6 mW/cm², about 1.4 mW/cm² to about 3.5 mW/cm², about 1.4 mW/cm² to about 3.4 mW/cm², about 1.4 mW/cm² to about 3.3 mW/cm², about 1.4 mW/cm² to about 3.2 mW/cm², about 1.4 mW/cm² to about 3.1 mW/cm², about 1.4 mW/cm² to about 3.0 mW/cm², about 1.4 mW/cm² to about 2.9 mW/cm², about 1.4 mW/cm² to about 2.8 mW/cm², about 1.4 mW/cm² to about 2.7 mW/cm², about 1.4 mW/cm² to about 2.6 mW/cm², about 1.4 mW/cm² to about 2.5 mW/cm², about 1.4 mW/cm² to about 2.4 mW/cm², about 1.4 mW/cm² to about 2.3 mW/cm², about 1.4 mW/cm² to about 2.2 mW/cm², about 1.4 mW/cm² to about 2.1 mW/cm², about 1.4 mW/cm² to about 2.0 mW/cm², about 1.4 mW/cm² to about 1.9 mW/cm², about 1.4 mW/cm² to about 1.8

[illegible]

[illegible]

[illegible]

seconds to about 90 seconds, of about 57 seconds to about 90 seconds, of about 58 seconds to about 90 seconds, of about 59 seconds to about 90 seconds, of about 60 seconds to about 90 seconds, of about 61 seconds to about 90 seconds, of about 62 seconds to about 90 seconds, of about 63 seconds to about 90 seconds, of about 64 seconds to about 90 seconds, of about 65 seconds to about 90 seconds, of about 66 seconds to about 90 seconds, of about 67 seconds to about 90 seconds, of about 68 seconds to about 90 seconds, of about 69 seconds to about 90 seconds, of about 70 seconds to about 90 seconds, of about 71 seconds to about 90 seconds, of about 72 seconds to about 90 seconds, of about 73 seconds to about 90 seconds, of about 74 seconds to about 90 seconds, of about 75 seconds to about 90 seconds, of about 76 seconds to about 90 seconds, of about 77 seconds to about 90 seconds, of about 78 seconds to about 90 seconds, of about 79 seconds to about 90 seconds, of about 80 seconds to about 90 seconds, of about 81 seconds to about 90 seconds, of about 82 seconds to about 90 seconds, of about 83 seconds to about 90 seconds, of about 84 seconds to about 90 seconds, of about 85 seconds to about 90 seconds, of about 86 seconds to about 90 seconds, of about 87 seconds to about 90 seconds, of about 88 seconds to about 90 seconds, of about 89 seconds to about 90 seconds, of about 30 seconds, of about 31 seconds, of about 32 seconds, of about 33 seconds, of about 34 seconds, of about 35 seconds, of about 36 seconds, of about 37 seconds, of about 38 seconds, of about 39 seconds, of about 40 seconds, of about 41 seconds, of about 42 seconds, of about 43 seconds, of about 44 seconds, of about 45 seconds, of about 46 seconds, of about 47 seconds, of about 48 seconds, of about 49 seconds, of about 50 seconds, of about 51 seconds, of about 52 seconds, of about 53 seconds, of about 54 seconds, of about 55 seconds, of about 56 seconds, of about 57 seconds, of about 58 seconds, of about 59 seconds, of about 60 seconds, of about 61 seconds, of about 62 seconds, of about 63 seconds, of about 64 seconds, of about 65 seconds, of about 66 seconds, of about 67 seconds, of about 68 seconds, of about 69 seconds, of about 70 seconds, of about 71 seconds, of about 72 seconds, of about 73 seconds, of about 74 seconds, of about 75 seconds, of about 76 seconds, of about 77 seconds, of about 78 seconds, of about 79 seconds, of about 80 seconds, of about 81 seconds, of about 82 seconds, of about 88 seconds, of about 84 seconds, of about 85 seconds, of about 86 seconds, of about 87 seconds, of about 88 seconds, of about 89 seconds, of about 90 seconds, or any range or value therebetween.

The photoinitiator catalyses the reaction of forming the network of crosslinked poly(ionic liquid) in the composite material. The photoinitiator may be selected from the group consisting of diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO), benzophenone, phenyl bis (2,4,6-trimethylbenzoyl)phosphine oxide, 2-hydroxy-2-methyl-1-phenyl-propan-1-one, 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone, 2,2'-azobis[2-methyl-n-(2-hydroxyethyl)propionamide], 2,2-dimethoxy-2-phenylacetophenone, lithium phenyl(2,4,6-trimethylbenzoyl)phosphinate), and ethyl (2,4,6-trimethylbenzoyl) phenylphosphinate.

Electrochromic Device

The composite material as disclosed herein may be used as an electrolyte. The composite material may be used as an electrolyte in electrochromic devices. The present invention further relates to an electrochromic device comprising an electrolyte sandwiched between two electrodes, wherein the electrolyte comprises the composite material disclosed herein.

The electrochromic device as disclosed herein may be illustrated in Figures 10, 13, 15, 16, 18, 21A, 21B, 22A, and 22B, comprising a composite material (which acts as an electrolyte) sandwiched between two electrodes.

The electrodes may be a fluorine-doped tin oxide (FTO) glass electrode, titanium dioxide (TiO₂) electrode, platinum (Pt) electrode, indium tin oxide (ITO) electrode, aluminium-doped zinc oxide (AZO) electrode as well as carbon nanotubes (CNT) electrodes, graphene electrode, conducting polymers electrode such as poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS)-based electrode and polyaniline (PANI)-based electrode, metal nanowires or metal mesh coated/embedded within glass or polymer substrates electrode.

The electrodes may be further coated with electrochromic materials such as organic or inorganic electrochromic materials as listed below.

The electrodes may be further coated with organic or inorganic electrochromic layers which can be:

(a) inorganic electrochromic materials such as tungsten oxide, molybdenum oxide, nickel oxide, vanadium oxide, iron oxide, titanium oxide, cobalt oxide, chromium oxide, copper oxide, iridium oxide, niobium oxide; and/or

(b) organic electrochromic materials such as viologens, viologen-derivatives, conducting polymers like Pedot:PSS, PANI, polythiophene, poly(3-hexylthiophene) (P3HT), poly(3,4-propylenedioxythiophene) (PProDOT), coordination complexes with different metals centers includes iron (Fe), ruthenium (Ru), osmium (Os), iridium (Ir), cobalt (Co), vanadium (V), nickel (Ni), and/or molybdenum (Mo).

The composite materials as disclosed herein may be used for organic electrochromic materials or inorganic electrochromic materials.

Method of Forming Electrochromic Device

Fabrication of electrochromic devices (ECDs) is to a great extent challenged by the composite material (or electrolyte component) as the preparation of gel

polymer electrolytes or ionogels has not been straightforward. Typically, hosting matrices are directly used in their polymeric form in a highly viscous mixture, which is inconvenient to handle and would be an issue upon upscaling. Upon incorporation or lamination of electrolyte in an ECD, the high viscosity could cause poor penetration of ionic species into the electrochromic active layer and could trap air bubbles upon fabrication, leading to poor interfacial contacts which adversely impact the device performance. Furthermore, some ionogels or composite materials were fabricated using a two-step ex-situ approach where swelling of cross-linked polymer network in ionic liquids is required after polymerization of monomers. Practicality wise, this two-step ex-situ approach is not favourable as deformation of polymer is likely to occur after the swelling process, making the dimensions of polymer difficult to control. In addition, conventionally, curing must be performed under an inert chamber with constant supply of inert gas which is undesirable and would restrict their applications.

In this present invention, an in-situ polymerization is employed which is an effective approach to improve the processability and enhance electrolyte contact, while maintaining the dimension of ionogels/composite materials. This approach uses liquid electrolyte comprised of heat- or light-curable monomers and crosslinkers that can be spontaneously processed into desired geometry. Unlike thermal polymerization process which requires substantial heat and a long curing duration (can be up to days), photopolymerization is much more facile and require lesser energy demand. Further, the curing of the method may be performed under ambient conditions, which enables a simple and easy process method with great compatibility with various applications.

The present invention relates to a method of forming an electrochromic device comprising: (i) applying a mixture of ionic liquid A, ionic liquid B, crosslinking agent, a photoinitiator, and optionally a metal borate complex between two electrodes; and (ii) curing the mixture with light irradiation, wherein the crosslinking agent reacts with ionic liquid B to form a polymer matrix comprising a network of crosslinked poly(ionic liquid B).

The method of forming an electrochromic device may be illustrated in Figure 10, where a mixture of ionic liquid A, ionic liquid B, crosslinking agent, a photoinitiator is applied to an electrode. The mixture may also comprise a metal borate complex.

The mixture may be applied by drop casting onto an electrode. By sandwiching the applied mixture with another electrode, the mixture undergoes self-wetting and is evenly spread in between the two electrodes. The mixture is then cured with light irradiation. The parameters used for the curing step is similar to that in step (ii) of the method of preparing composite material. With the curing of the mixture performed when the mixture is sandwiched in between the electrodes, the mixture undergoes in-situ polymerization to form the composite material.

Upon irradiation, the crosslinking agent reacts with ionic liquid B to form a polymer matrix comprising a network of crosslinked poly(ionic liquid B). Through the irradiation, the network of crosslinked poly(ionic liquids) in the composite material is formed which serve as the stationary phase to anchor ionic liquid A and eventually form the composite material of a resulting electrochromic device. The electrochromic device is formed with a composite material (which acts as an electrolyte) sandwiched in between the two electrodes.

For step (ii), the irradiated light may be of a wavelength of about 300 nm to about 500 nm. Step (ii) may be performed at an irradiance of about 1.4 mW/cm^2 to about 4.2 mW/cm^2 . Step (ii) may be performed for a duration of about 30 seconds to about 90 seconds.

The composite materials as disclosed herein may be used for organic electrochromic materials or inorganic electrochromic materials. The assembled electrochromic device may display high colour contrast and fast response time with good endurance over thousands of switching cycles and exhibit great performance as an electrochromic device. The composite materials of the present invention may display colour-switching properties in response to changes in temperature or changes in applied current/potential while still retaining its state and form.

Changes in temperature may cause an effect on the composite materials of the present invention. Hot or cold temperature applied on the composite material may cause a change in chemical oxidation states of the composite material and result in colour switching in the transmissive displays of the composite material. When temperature is applied, the composite materials may switch colours, while still retaining the state and form of the composite material.

Further, current and/or potential applied on the composite material may cause an effect on the composite material of the present invention. When current/potential is applied on the composite material, the chemical oxidation states of the composite material changes and the colour of the composite materials may change. The composite material may be used in both reflective and transmissive electrochromic displays. When current or potential is applied to the composite material, the composite materials may switch colours but still retain their state and form. In another embodiment, flexing and twisting motions of the composite material when current or potential is applied may not affect the colour switching process.

In an embodiment, the polymer matrix of the composite material comprises a metal-ion-containing polymer backbone (for example, an Li-ion-containing polymer backbone). The composite material may further comprise a plasticizer (for example, propylene carbonate). The metal-ion-containing polymer backbone serves as a metal-ion source and together with the plasticizer, facilitate metal-ion transportation.

Statements of Invention

Some statements of the present invention are as follows:

1. A composite material comprising:
an ionic liquid A; and
a polymer matrix comprising a network of crosslinked poly(ionic liquid B).
2. The composite material of statement 1, wherein the polymer matrix is formed by reaction of an ionic liquid B with a crosslinking agent.
3. The composite material of statement 1 or 2, wherein ionic liquid A and ionic liquid B are different.
4. The composite material of any one of statements 1 to 3, wherein ionic liquid A and ionic liquid B each comprise a cation selected from the group consisting of ammonium, cholinium, imidazolium, isoquinolinium, oxazolium, phosphonium, piperidinium, pyrazinium, pyridinium, pyrimidinium, and pyrrolidinium.
5. The composite material of any one of statements 1 to 4, wherein ionic liquid A and ionic liquid B each comprise an anion selected from the group consisting of acetate, benzenesulphonate, bistriflimide, dicyanamide, dihydrogenphosphate, formate, halide, hexafluorophosphate, hydroxide, lactate, nitrate, tetrachloroferrate, tetrafluoroborate, tricyanomethanide, and triflate.
6. The composite material of any one of statements 1 to 5, wherein ionic liquid A comprises a cation substituted at least once with C₁ to C₁₀ alkyl.
7. The composite material of any one of statements 2 to 6, wherein ionic liquid B comprises a cation substituted at least once with C₂ to C₁₀ alkene.
8. The composite material of any one of statements 2 to 7, wherein the crosslinking agent comprises acrylate groups.
9. The composite material of statement 7 or 8, wherein the polymer matrix is formed by reaction of the alkene of ionic liquid B with the acrylate of the crosslinking agent.
10. The composite material of any one of statements 1 to 9, further comprising a metal borate complex.
11. The composite material of any one of statements 2 to 10, wherein
the ionic liquid A is 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (EMIMTFSI);
the ionic liquid B is 1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl) imide (BVIMTFSI); and
the crosslinking agent is poly(ethylene glycol) diacrylate (PEGDA).

12. The composite material of statement 10, wherein
the ionic liquid A is 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (EMIMTFSI);
the ionic liquid B is 1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl) imide (BVIMTFSI);
the crosslinking agent is poly(ethylene glycol) diacrylate (PEGDA); and
the metal borate complex is lithium methacrylate trifluoroborate complex in propylene carbonate.
13. The composite material of any one of statements 1 to 12, wherein the composite material is an ionogel.
14. The composite material of any one of statements 1 to 13, wherein the composite material has a transmittance of about 90% to about 98% at 1 mm thickness.
15. The composite material of any one of statements 1 to 14, where the composite material has a crosslink density of about 0.02 mol/g to about 0.05 mol/g, or 0.035 mol/cm³ to about 0.06 mol/cm³.
16. A method of preparing a composite material of any one of statements 1 to 15, comprising the steps of:
 - (i) preparing a mixture of ionic liquid A, ionic liquid B, crosslinking agent, and a photoinitiator;
 - (ii) curing the mixture with light irradiation,
wherein the crosslinking agent reacts with ionic liquid B to form a polymer matrix comprising a network of crosslinked poly(ionic liquid B).
17. The method of statement 16, wherein step (i) further comprises adding a metal borate complex.
18. The method of statement 16 or 17, wherein step (ii) is performed for a duration of about 30 seconds to about 90 seconds.
19. The method of any one of statements 16 to 18, wherein the photoinitiator is selected from the group consisting of diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO), benzophenone, phenyl bis (2,4,6-trimethylbenzoyl)phosphine oxide, 2-hydroxy-2-methyl-1-phenyl-propan-1-one, 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone, 2,2'-azobis[2-methyl-n-(2-hydroxyethyl)propionamide], 2,2-dimethoxy-2-phenylacetophenone, lithium phenyl(2,4,6-trimethylbenzoyl)phosphinate), and ethyl (2,4,6-trimethylbenzoyl) phenylphosphinate.
20. An electrochromic device comprising an electrolyte sandwiched between two electrodes, wherein the electrolyte comprises the composite material of any one of statements 1 to 15.

21. A method of forming an electrochromic device comprising:

- (i) applying a mixture of ionic liquid A, ionic liquid B, crosslinking agent, a photoinitiator, and optionally a metal borate complex between two electrodes; and
- (ii) curing the mixture with light irradiation,

wherein the crosslinking agent reacts with ionic liquid B to form a polymer matrix comprising a network of crosslinked poly(ionic liquid B).

22. The composite material of statement 6, wherein ionic liquid A comprises a cation substituted twice with C₁ to C₁₀ alkyl.

23. The composite material of statement 7, wherein ionic liquid B comprises a cation substituted with C₁ to C₁₀ alkyl and C₂ to C₁₀ alkene.

24. The composite material of statement 23, wherein ionic liquid B comprises an imidazolium cation substituted with C₁ to C₁₀ alkyl and C₂ to C₁₀ alkene.

Examples

Non-limiting examples of the invention and a comparative example will be further described in greater detail by reference to specific examples, which should not be construed as in any way limiting the scope of the invention.

Reagent and Materials

Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, >98%), 1-vinylimidazole (>98%), and 1-bromobutane (>98%) were purchased from Tokyo Chemical Industry (TCI) Chemicals. 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIMTFSI, ≥98), Poly(ethylene glycol) diacrylate (PEGDA700, M_n 700), diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO, 97%), methacrylic acid (99%), lithium hydroxide (>99%), Boron trifluoride tetrahydrofuran complex (BF₃.THF) and propylene carbonate (PC, >99.7%) were procured from Sigma-Aldrich. Lithium methacrylate (LiMA) was prepared by reacting methacrylic acid and lithium hydroxide. TiO₂ paste (18NR-T, Greatcell Solar materials) was purchased and used to coat the counter electrode. Diethyl ether (Schedelco) and ethyl acetate (Fisher Scientific) were of analytical or HPLC grade and were used as received. Fluorine-doped tin oxide (FTO) coated glass used after cleaning with H₂O, acetone, and isopropyl alcohol.

Characterization Techniques and Measurements

Nuclear Magnetic Resonance (NMR) spectroscopy

^1H NMR spectra were obtained from Bruker Avance DPX-400 (400 MHz) Fourier-transform NMR spectrometer at 298 K and calibrated against tetramethylsilane, $\text{Si}(\text{CH}_3)_4$.

Fourier-Transform Infrared (FTIR) Spectroscopy

All FTIR spectra were collected in the wavenumber range of 4000-600 cm^{-1} using a PerkinElmer Fourier Transform Infrared (FTIR) Frontier spectrometer with attenuated total reflection (ATR) accessory, which average over 32 scans at a resolution of 4 cm^{-1} .

Thermogravimetric Analysis (TGA) & Differential Scanning Calorimetry (DSC)

Thermal stability of the composite materials was determined by TGA through ramping the temperature from room temperature to 700 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C min}^{-1}$. DSC was used to determine the glass transition temperature (T_g) and melting temperature (T_m) of the composite materials by cooling/heating at 10 $^{\circ}\text{C min}^{-1}$.

Contact Angle (CA) and Surface Tension (γ) Measurements

DataPhysics OCA 15PRO goniometer was used to measure contact angle (CA) and surface tension (γ). CA measurements were performed using the static sessile drop method. A 1.5 μL droplet of liquid ink was dispensed at a dosing rate of 0.5 $\mu\text{L s}^{-1}$ using a Hamilton microsyringe and deposited on top of the substrate surface. The captured images and videos of the droplet were then analyzed to retrieve the CA values.

γ measurements were performed using the pendant drop method. The camera was turned 90 $^{\circ}$ to allow greater zoom-factor and detection of the drop contour. The pendant drop of the sample was dispensed as big as possible and was analyzed with necessary information (phase density, needle size, etc.) to retrieve the γ value.

Ultraviolet – Visible (UV-Vis) Spectroscopy

The electronic absorption spectra in this work were acquired using a Perkin Elmer Lambda 950 spectrophotometer in transmittance mode. In-situ spectroelectrochemical measurements were performed by applying potential using an Autolab PGSTAT302 N Potentiostat/Galvanostat.

Electrochemical Measurements

All electrochemical experiments and characterization such as cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and chronoamperometry (CA) were performed using an Autolab PGSTAT 302N Potentiostat/Galvanostat. EIS information was obtained by applying an AC voltage of 5mV amplitude spanning a frequency range between 0.1 and 100k Hz.

Ionic Conductivity Measurements

Ionic conductivity of the composite materials was derived using the equation $\sigma = l/RA$ in a sandwich configuration with two metal plates as electrodes. (R is the measured impedance, l and A are the thickness and cross-sectional area of the composite materials, respectively). Temperature-dependent ionic conductivity measurements were carried out in an electric oven or a refrigerator at -20, 0, +20, +40, +60, +80, +100 °C by storing the sample inside for an hour.

Preparation of Composite Materials (CM A and CM B)

In the present invention, two composite materials, denoted as CM A and CM B, were prepared. CM A is being formulated to target organic electrochromic materials, such as viologens, coordination compounds, and conducting polymers, which only require electrolytes for charge-balancing purposes. On the contrary, CM B is tailor-made for inorganic electrochromic materials, for example like WO_3 , NiO , and V_2O_5 , where intercalation of ion is imperative.

The two in-situ polymerized ionogels (CM A and CM B) can be rapidly cured within a minute. The main difference between the two composite materials is that CM B accommodates additional lithium-ion-containing polymer backbone and propylene carbonate (PC), serving as Li-ion source and plasticizer, respectively. The additional Li-ion-containing polyanionic moiety and propylene carbonate (PC) as plasticizer facilitate Li-ion transportation.

The preparation of two highly transparent and flexible ionogels (denoted as CM A and CM B) is illustrated in examples 1-3. Examples 2-3 also illustrate the preparation via rapid photopolymerization under ambient conditions. The preparation of a precursor of CM A and CM B, which is 1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide (BVIMTFSI), is illustrated in Example 1, and the composition of CM A and CM B precursor mixtures is depicted in Figures 1A and 1B.

Example 1: Preparation of a Precursor of CM A and CM B

1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide (BVIMTFSI) was prepared via a two-step reaction as shown in examples 1(a) and 1(b).

Example 1(a):

1-butyl-3-vinylimidazolium bromide (BVIMBr)

1-bromobutane (76.4 g, 0.558 mol) was added dropwise to a solution of 1-vinylimidazole (50.0 g, 0.531 mol) over a period of 2 hours and stirred at 40 °C for 24 hours.

The resulting viscous liquid was washed with ethyl acetate three times and precipitate in diethyl ether. White precipitate was then collected and dried in vacuo.

NMR spectroscopy was conducted on the sample (white precipitate) to yield the following: yield: 116.6 g, 0.504 mol, 95%. ^1H NMR (400 MHz, CDCl_3 , 298K, δ / ppm): δ 10.97 (s, 1H), 7.88 (t, $J = 1.8$ Hz, 1H), 7.61 (t, $J = 1.8$ Hz, 1H), 7.51 (dd, $J = 15.6, 8.8$ Hz, 1H), 6.02 (dd, $J = 15.6, 3.0$ Hz, 1H), 5.41 (dd, $J = 8.8, 3.0$ Hz, 1H), 4.43 (t, $J = 7.4$ Hz, 2H), 1.96 (quintet, 2H), 1.22 (sextet, 2H), 0.98 (t, $J = 7.4$ Hz, 3H). Figure 2 (a) shows the ^1H NMR spectrum of BVIMBr in CDCl_3 .

Example 1(b):

1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide (BVIMTFSI)

The white product, BVIMBr (50.0 g, 0.216 mol) was then stirred in a solution of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 68.3 g, 0.238 mol) in 50 mL of water (H_2O) and stirred for 24 hours. Afterwards, 3 x 50 mL of CH_2Cl_2 was used to extract the product which are then dried in vacuo to yield pale yellow liquid.

NMR spectroscopy was conducted on the sample (i.e., pale yellow liquid) to yield the following: yield: 59.6 g, 0.180 mol, 83%. ^1H NMR (400 MHz, CDCl_3 , 298K, δ / ppm): δ 9.06 (s, 1H), 7.61 (t, $J = 1.8$ Hz, 1H), 7.42 (t, $J = 1.8$ Hz, 1H), 7.14 (dd, $J = 15.6, 8.7$ Hz, 1H), 5.78 (dd, $J = 15.6, 3.0$ Hz, 1H), 5.44 (dd, $J = 8.7, 3.0$ Hz, 1H), 4.24 (t, $J = 7.5$ Hz, 2H), 1.89 (quintet, 2H), 1.39 (sextet, 2H), 0.97 (t, $J = 7.5$ Hz, 3H). Figure 2 (b) shows the ^1H NMR spectrum of BVIMTFSI in CDCl_3 .

Example 2: Preparation of Composite Material A (CM A)

CM A precursor mixture was prepared by mixing 1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide (BVIMTFSI, 1000mg), poly(ethylene glycol) diacrylate (PEGDA, average M_n 700, 25 mg), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIMTFSI, 600 mg) and diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO, 25 mg) using a vortex mixer and sonicated for 15 minutes to remove the air bubble. The preparation may be scaled up accordingly to the respective ratio if needed.

The CM A precursor mixture was then cured under 395 nm light irradiation (2.8 mW cm^{-2}) for one minute, affording a transparent flexible film. Figure 3 shows the mechanism of (a) photoinitiation and (b) chain-mode radical photopolymerization.

Example 3: Preparation of Composite Material B (CM B)

CM B precursor mixture was formulated to incorporate lithium (Li^+) ion source, with addition of 10 weight % of lithium methacrylate trifluoroborate complex solution (LiMABF_3 , 2 M in propylene carbonate) LiMA (2 M in PC) into CM A precursor mixture (as mentioned in Example 2).

LiMABF_3 solution was prepared by adding equivalent amount of lithium methacrylate (LiMA) and boron trifluoride tetrahydrofuran ($\text{BF}_3\cdot\text{THF}$) complex in anhydrous propylene carbonate (PC) and stirred for 2 hours. For example, 2.0 M of LiMABF_3 in PC was prepared by adding equivalent amount of $\text{BF}_3\cdot\text{THF}$ (700 mg, 5 mmol) into LiMA (460 mg, 5 mmol) in PC (2.5 mL) and stirred for 2 hours. This solution is stored in a 4 °C refrigerator. This solution mixture needs to be kept inside a fridge (i.e., 4 °C refrigerator) if it is not used instantly.

The CM B precursor mixture was then cured under 395 nm light irradiation (2.8 mW cm^{-2}) for a minute, affording a transparent flexible film for various applications. Figure 3 shows the mechanism of (a) photoinitiation and (b) chain-mode radical photopolymerization.

By one-step photopolymerization of vinyl-functionalized ionic liquids (namely BVIMTFSI) and acrylate-terminated crosslinking agents (namely PEGDA700), a network of interlinked poly(ionic liquids) in the composite material is formed which serve as the stationary phase to anchor the ionic liquid mobile phase (namely 1,3-ethylmethyylimidazolium bis(trifluoromethylsulfonyl)imide, EMIMTFSI). To ensure high mobility, miscibility, and compatibility of the ionic liquid with the polymer backbones, bis(trifluoromethylsulfonyl)imide (TFSI) anion which behaves as a weakly or non-coordinating anion has been used.

Due to its large size and charge delocalization, TFSI anions lead to relatively weak binding with cations, resulting in not only higher conductivity but also lower freezing temperature than other counter anions (Cl , Br , BF_4 & PF_6), allowing it to operate at sub-zero temperature. TFSI anions also exhibit the highest hydrophobicity relative to other anions (Br , BF_4 , NO_3 , ClO_4 , CF_3SO_3 & PF_6), which could minimize the influence of water in an electrochemical device or electrochromic device (ECDs).

Characterization of Composite Materials (CM A and CM B)**Example 4: Loading of EMIMTFSI per gram of BVIMTFSI**

Each component in the precursor mixtures is rationally selected so that they are miscible and can be readily prepared via a simple mixing process. These formulations were first optimized based on the loading fraction of EMIMTFSI (mobile phase).

Optimization of conductivities of cured composite material based on loading/fraction of EMIMTFSI was conducted and a plot of $\log \sigma$ with respect to loading of EMIMTFSI is shown in Figure 4. Table 1 summarizes the ionic conductivity variation with the loading of EMIMTFSI. As shown in Figure 4 and Table 1, ionic conductivity increases with the loading of EMIMTFSI and plateau off beyond 60 weight percent (wt. %) EMIMTFSI loading per gram of BVIMTFSI.

Table 1. Optimization of conductivities of cured composite material based on loading of EMIMTFSI (i.e., ionic conductivity variation with the loading of EMIMTFSI).

Loading of EMIMTFSI per gram of BVIMTFSI	Ionic conductivity (S/cm)
0	2.50×10^{-5}
30 wt. %	1.23×10^{-3}
60 wt. %	2.67×10^{-3}
90 wt. %	3.89×10^{-3}
120 wt. %	3.98×10^{-3}

Based on the results in Figure 4 and Table 1, 60 wt. % EMIMTFSI has been selected in this present invention to keep the mobile phase minimally to maintain the integrity of the prepared solid film. An intriguing observation is that without the addition of the mobile phase, the morphology of the composite material would manifest a chain-like microstructure (as shown in Figure 5 – Scanning Electron Microscope (SEM) images of (a) CM without addition of mobile phase (Bare CM), (b) CM A, and (c) CM B). This suggests that the mobile phase is essential as it reduces intervals and micropores between the polymer molecule chains caused by phase separation, allowing better electrode-electrolyte interface.

Example 5: Photopolymerization and FTIR Characterization of CM A and CM B

Photopolymerization has been employed to prepare the composite materials as curing under light is usually much more rapid, and it would give better spatial control compared to the thermal curing process.

Photopolymerization of both CM A and CM B was directly monitored using Fourier-Transform Infrared (FTIR) spectroscopy under ambient conditions. Figures 1A and 1B show the composition of composite materials CM A and CM B and their respective time-dependent FT-IR spectra which indicates that the polymer can be cured within a one-minute timeframe.

As shown in Figures 1A and 1B, C=C stretching band (at ca. 1650 cm^{-1}) and C=C twisting vibrational band (at ca. $1000\text{-}900 \text{ cm}^{-1}$) decrease upon exposure to light at 395 nm. In addition, the characteristic stretching band of C=O from the acrylate

group of PEGDA also shifted from 1720 to 1731 cm^{-1} which is in line with the changes from α,β -unsaturated ester to saturated ester groups during polymerization.

In both composite materials, unsaturated bonds are completely depleted throughout 50 seconds of light exposure (395 nm, 2.80 mW cm^{-2}), indicative of a rapid preparation of crosslinked composite materials, even in the presence of ambient oxygen. After photopolymerization, the composite materials would be in solid state (Figure 6A), and no other steps are required to confine the electrolyte.

The polymerizable functional groups in the formulation such as vinyl and acrylates group were fully depleted when a 395 nm light was used to initiate the radical polymerization process. The preparation process is facile and therefore guarantees excellent reproducibility of the physicochemical and electrochemical properties.

Due to high miscibility of every component within the composite materials, the cured CM A and CM B are highly transparent over a broad spectral range from 380 to 1250 nm, particularly, the transmittance could reach up to 98% at 1 mm thickness (Figure 6B).

Example 6: Thermal Properties of Composite Materials CM A and CM B

Electrochromic devices (ECDs) are widely used in various environments including under scorching hot weather so it is critical to understand the thermal stabilities of the prepared composite materials (which can be used as an electrolyte in electrochromic devices).

Thermal properties of CM A and CM B were evaluated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) as shown in Figures 7A and 7B respectively. The thermal stabilities of both composite materials and their individual components were evaluated by thermogravimetric analysis (TGA), as shown in Figure 7A and Figure 8. The TGA of CM A reveals that it is stable up to 357 °C with less than 3% weight loss, beyond which it decomposed in a one-step process. On the other hand, CM B shows loss of weight in two stages at 203 °C and 357 °C, which can be attributed to the evaporation of PC plasticizer and degradation of the polymer backbones, respectively. According to the results and figures described, the result of high thermal stabilities suggests that both composite materials are functional even in an extremely hot environment.

Molecular flexibility of the polymer chain could affect not only the ions mobility but also the rigidity of the crosslinked composite material. To gain insight into the polymer dynamics, differential scanning calorimetry (DSC) ramp analyses have been performed to reveal both the glass transition temperature (T_g) and melting temperature (T_m) of the composite material (Figure 7B). From the DSC, CM A and CM B manifested a sub-zero T_g at -67.8 and -74.7 °C, respectively. The slight reduction of T_g of CM B relative to CM A is due to the plasticizer effect of the PC, which afforded the polymer with higher chain mobility. The fact that only one T_g is observed in both CM A and CM

B indicates that the ionogels are highly homogeneous without any phase separation. In addition, both CM A and B show a T_m at ca. $-17.0\text{ }^{\circ}\text{C}$, which is in line with the T_m of the EMIMTFSI mobile phase.

Example 7: Transmittance of Composite Materials (CM A and CM B)

Apart from ionic conductivity, electrolytes that are used in electrochromic devices (ECDs) need to have high transparency and possess good thermal-electrochemical stabilities.

Due to high miscibility of every component within the composite materials, the cured CM A and CM B are highly transparent (Figure 6B), particularly, transmittance can reach up to 98% (at 1 mm thickness) over the entire visible spectrum (380 to 780 nm) as well as the in part of the near-IR regime (780 to 1250 nm). This transmittance value is better than conventional borosilicate glass which has a transmittance value of around 92% (at 1 mm thickness). In the event that the thickness of the composite materials is further reduced, these electrolytes can attain virtually 100% transmittance which is highly desired for their application in ECDs.

Example 8: Electrochemical Measurements of Composite Materials

One of the key advantages of using ionic liquids in composite materials is that they could offer a wide electrochemical window, which translates to better electrochemical stability. In this context, the electrochemical stability of composite materials was investigated by using symmetric Fluorinated Tin Oxide (FTO) electrodes in relation to EMIMTFSI.

From electrochemical stability measurements in Figure 7C, CM A, and CM B displayed a stable potential window of ca. $\pm 2.4\text{ V}$, and $\pm 2.2\text{ V}$ at an arbitrary cut-off value of 0.01 mA cm^{-2} . The measured value of EMIMTFSI is comparable. Thus, with measured value of EMIMTFSI, it can be determined that the working potential of the composite materials has been confined within the voltage range for prolonged stability.

Example 9: Ionic Conductivity Measurements of Composite Materials

The ionic conductivity of both composite materials CM A and CM B has also been measured over wide temperature range from -20 to $100\text{ }^{\circ}\text{C}$ (Figure 7D), showing that the conductivities increase with temperature and follows a Vogel-Tamman-Fulcher behaviour.

While preparation of highly ionic conductive composite materials that is functional at both low and high temperatures remains a challenge, it is sought-after for high-performance ECDs. Figure 7D shows variation of ionic conductivity of the composite materials as a function of reciprocal temperature from -20 to 100 °C. From the plot, the ionic conductivity of the composite materials increases with temperature because of faster ions movement. Unlike conventional liquid salt electrolyte which follows an Arrhenius linear relation with temperature, the non-linearity temperature dependency of the ionic conductivity of the ionogels can be described by the Vogel-Tamman- Fulcher (VTF) equation: $\sigma T^{1/2} = A \exp(-\frac{B}{T-T_0})$, where A is associated with the amount of charge carrier in the electrolyte, B is related to activation energy of ionic movement and T_0 (Vogel temperature) is the ideal glass transition temperature at which the polymer mobility or conductivity drops to zero. The VTF description is also in agreement with the free volume theory, which can explain the conductivity difference between CM A and CM B.

As demonstrated in Figure 7B, CM B has a lower glass transition temperature relative to CM A. This implies a more flexible chain between the chemical junctions in the loose CM B network, which facilitate greater mobility of ions and thereby, CM B exhibits a higher ionic conductivity over the entire temperature range. Unlike hydrogel which loses its desired ionic properties once temperature exceeded its boiling point or dropped below its freezing point, the achievement of high ionic conductivity of solid-state ionogels over a wide temperature makes them a promising electrolyte to be used in flexible ECDs which seepage of electrolytes can be prevented under different working environments.

Example 10: Preparation of Working and Counter Electrodes

The prepared composite materials (CM A and CM B) are highly transparent, flexible, and exhibit excellent physicochemical stability, including thermal stability, electrochemical stability, and air stability, allowing them to perform in various conditions.

Benefitting from these properties, high-performance electrochromic devices can be assembled. Working electrodes can either be coated with organic or inorganic electrochromic materials. As shown in the examples below, an organic iron coordination polymer can be electropolymerized on an FTO electrode to form the working electrode (Example 10(a)); and an inorganic electrochromic electrode, such as tungsten oxide, WO_3 , can be coated onto FTO electrode via inkjet printing or spray-coating method (Example 10(b)). CM A ionogel is used for organic electrochromic materials, while CM B is used for inorganic electrochromic materials.

Example 10(a): Preparation of Fe-CP Working Electrodes

Fe-CP was coated onto the FTO glass by electropolymerization method. However, the Fe-CP may also be coated onto the FTO glass by spray coating, electrostatic spraying, dip coating, and spin-coating. By using the FTO working electrode, Pt counter electrode and Ag/Ag⁺ reference electrode, 20 potentiodynamic cycles (0 to 1.3 V at 100 mV s⁻¹) was applied in a solution of 1 mM of [Fe(tpyPhNH₂)₂](PF₆)₂ mixed with 0.1 M TBAP in acetonitrile. After that, the as-prepared electrode was cleaned by sonicating the electrode in acetonitrile for 30 seconds.

Example 10(b): Preparation of P-WO₃ Working Electrodes

The WO₃ nanoparticles were first prepared by direct oxidation of tungsten (W) nanoparticles with hydrogen peroxide solution via a vigorous stirring process. The obtained WO₃ nanoparticles were then freeze-dried and dispensed in a mixture of solvent (1:1 mixture of water and diethylene glycol n-butyl ether (DOWANOL DB)), without sonication, and with heating, filtration, and addition of dispersing agents to form an ink formulation. The WO₃ film were inkjet printed on the FTO glass and dried at 60 °C for 2 hours. PEDOT:PSS/WO₃ electrodes were prepared by spray-coating the diluted PEDOT:PSS (1 ml of 0.5 % PEDOT in H₂O per cm²) on the as prepared WO₃/FTO electrode.

To counteract the rather sluggish kinetics of WO₃ in solid state electrolyte, a thin layer of PEDOT:PSS has been coated onto WO₃ (denoted as P-WO₃) to promote electron transportation.

Example 10(c): Preparation of TiO₂ Counter Electrodes

Commercial TiO₂ paste was coated by using a micro groove coater with groove depth of 75 μm (Kaivo), followed by a sintering process at 500 °C for 2 hours. This resulted in an even distribution of anatase (size of 20 nm) at a thickness of *ca.* 8 μm.

On the counter electrode, non-electrochromic TiO₂ nanoparticles, which are known to lower working voltage and prolong cycling stability, were adopted as the charge-balancing layer (Figure 9A and Figure 9B). Figure 9A shows a SEM image of TiO₂ NP coated FTO electrode and Figure 9B shows the spectral transmittance of TiO₂ NP coated FTO electrode.

Example 11: Fabrication of Electrochromic Devices (ECDs)

In this invention, the inventors show that composite materials CM A and CM B can be utilized as the electrolyte of ECDs in electrochromic applications, targeting both organic and inorganic materials. Benefitting from the inherent properties of the disclosed composite materials, the as-prepared CM A and CM B were employed as electrolytes for

ECDs based on organic iron-centered coordination polymer (Fe-CP) and inorganic tungsten oxide (WO₃), respectively.

The fabrication steps of an ECD are depicted in Figure 10, to which working and counter electrodes were used to sandwich the composite material in between. An ECD is fabricated by sandwiching the composite material (10 $\mu\text{L}/\text{cm}^2$) in between the as-prepared working and counter electrodes. This is then followed by one minute of curing process under light exposure at 395 nm. The free edges of these substrates were then affixed with conductive copper tape to conform a reliable electrical connection.

In the present invention, sandwich ECDs were fabricated through a combination of self-wetting process and in-situ photopolymerization (Figure 10). To gain insight into the spreading or wettability of the precursor mixture, their surface tensions (γ_{la}) and static contact angles (θ_{st}) were evaluated using an optical goniometer. By using the pendant drop method, the derived γ_{la} of CM A and CM B precursor mixture are *ca.* 29.2 and 29.6 mN/m (Figures 11A and 11B). These low γ_{la} values indicate that the precursor mixture have a relatively low cohesion or poor attraction between the components in the ink solution. Hence, this would allow better spreading of the precursor ink onto the surface of the electrode.

Other than the surface tension γ_{la} , the wettability is dependent on the chemical nature and topographic properties of the substrate surface. This factor was revealed by θ_{st} measurements, which are summarized in Table 2. It is noteworthy that both precursor inks exhibit contact angles of less than 20° on both electrochromic and counter substrates, indicative of a good spreading tendency.

Table 2. Contact angle measurement of composite materials CM A and CM B on different substrates.

Composite Material	Bare FTO	TiO ₂ /FTO	FeCP/FTO	P-WO ₃ /FTO
CM A	28.1	19.5	3.4	-
CM B	19.7	12.5	-	18.9

Taking the advantage of this property, an ECD could be readily fabricated by sandwiching the electrolyte between the substrates as depicted in Figure 10. The precursor mixture would readily spread out when another electrode is placed on top, forming a uniform interlayer. This is then followed by the photopolymerization process for solidification and adherence. By adopting this wetting behaviour, the thickness of the electrolyte can be readily controlled by the volume of deposited precursor mixtures (as shown in Figure 12), avoiding the use of spacers. 10 $\mu\text{L}/\text{cm}^2$ of precursor mixture has been applied to the designated electrochromic active surface for assessment of the electrochromic performance of composite materials.

Example 12: Fabrication of ECD based on organic iron coordination polymer (FeCP) and its performance

To assess the performance of the composite materials in ECDs, CM A and CM B are separately constructed into devices and evaluated via spectroelectrochemical analysis. CM A has been used and assembled into an ECD based on FeCP and TiO₂ NP electrodes as shown in Figure 4. CM A was used as the electrolyte to fabricate an ECD with FeCP working electrode and TiO₂ counter electrode. The actual photograph of the device is shown in Figure 13.

Over the cyclic potential range between +0.5 and +2.5 V (Figure 14A), the FeCP device exhibited a pronounced redox couple which is known to originate from the oxidation of Fe²⁺ and reduction of Fe³⁺ metal centres. It is notable that without the TiO₂ counter electrode, the redox peaks would be drifted far apart, affecting not only the reversibility of the system but also the widen the required switching potential (Figure 15).

During this electrochemical activity, the device changes between a coloured purplish-blue state and a bleached transparent state, as a result of the metal-to-ligand charge transfer (MLCT) suppression. From the spectroelectrochemical measurement (Figure 14B), optical contrast ($LIT = Tb - Tc$) of as high as 45.2% could be attained at 572 nm with fast switching response of $tb = 1.5$ s and $tc = 1.9$ s (Figure 14C). Prolonged stability test in Figure 14D illustrated that the device was able to retain about 94.6% of its initial LIT after 3000 chronoamperometric switching cycles.

Although the response time is somewhat slower than the value of <1s, the times needed for coloration and bleaching are still considered rapid as a solid-state electrolyte was being used instead of liquid electrolyte. The electrochromic endurance of the FeCP device was also evaluated via changes in transmittance (at 572 nm) as a function of switching cycles. It was found that the device was able to retain about 94.6% of its initial LIT after 3000 chronoamperometric switching cycles. The cycling stability is thus determined to be much better than in liquid electrolyte, probably due to the use of solid-state ionogel that could hold the electrochromic film in place, preventing delamination at the electrode surface.

Example 13: Fabrication of ECD based on inorganic tungsten oxide (P-WO₃) and its performance.

Correspondingly, CM B with the additional lithium-ion source has also been used in fabricating an ECD based on P-WO₃ and TiO₂ electrodes as shown in Figure 4. Similar to Example 12, the ECD based on inorganic WO₃ working electrode and TiO₂ counter electrode was fabricated with the composite material CM B based on the step shown in Figure 4. The actual photograph of the device is shown in Figure 16.

Over the cyclic potential range between -2.0 and +2.0 V (Figure 17A), the P-WO₃ device displayed a well-defined redox couple which comes from the reduction of W⁶⁺ to W⁵⁺ through electron insertion alongside concomitant Li-ion intercalation.

Similar to the FeCP device, the P-WO₃ device showed distorted redox peaks and a wider potential range without TiO₂ counter electrode (Figure 18). This again reaffirmed the importance of having a charge-balancing layer. When the device is in operation, the Li⁺ ions are driven into the WO₃ layer, causing it to change from colourless to dark blue.

From Figures 17B and 17C, spectroelectrochemical measurement of the P-WO₃ device shows that it could attain a high optical contrast ($LIT = Tb - Tc$) of 56.4% at 660 nm with switching response of $tc = 1.7$ s and $tb = 6.4$ s. The device has also been assessed under prolonged colour switching cycles (Figure 17D), showing contrast retention of 93.2% at 3000 cycles and 84.3% at 5000 cycles.

In addition, to illustrate the thermal robustness of the composite material, the P-WO₃ device was also examined under two temperature extremes, namely -20 and 100 °C. From the chronoamperometric (or current-time) measurements, the amount of charges upon switching is larger at higher temperature (Figure 19B).

This can be ascribed to accelerated redox kinetics at elevated temperature due to better ion mobilities. From the transmittance spectra (Figure 19C), the device at -20 °C shows a drop in contrast to *ca.* 65% of its initial contrast at 20 °C, likely due to impeded ion movement at sub-zero temperature. While at 100 °C, the device shows a slight increment in contrast relative to its 20 °C counterpart.

This result agrees well with the inherent thermal properties of composite materials, allowing the fabricated ECDs to operate at a wide temperature range, unlike hydrogel-based electrolytes that are limited by the freezing and boiling temperature of water.

Example 14: Compatibility of the Composite Materials with Various Deformable Substrates and Use of Composite Materials as Flexible Electrochromic Eye Protector and Displays

To translate the use of ionogels into flexible ECDs, deformable substrates such as ultra-thin ITO glass, Ni-Cu conductive textile and ITO-PET were employed to realize flexible P-WO₃ devices. Unlike ITO on polymer substrates, which would usually give very different properties than its glass counterpart, ultra-thin ITO glass offer a new possibility to directly transfer the electrochromic performance from a rigid device to a flexible one. To demonstrate the compatibility of the ultra-thin glass with the ionogel, a curved eyes protector has been fabricated as shown in Figure 20 which exhibited essentially similar spectroelectrochemical performance as the rigid P-WO₃ device. Figure 20 shows the change in colour and also change in state from transparent (bleached) to transmissive coloured state when a current/potential of +1.5V and to -2.0V is applied to the curved

electrochromic device (ECD) based on ultra-thin ITO glass switching. It is observed that when -2.0V is applied, the curved electrochromic device (ECD) based on ultra-thin ITO glass switching is coloured, and allows partial visualization while at +1.5V, the curved electrochromic device (ECD) based on ultra-thin ITO glass switching is bleached and transparent.

Both reflective and transmissive electrochromic displays have also been manifested in Figures 21A-B and Figures 22A-B respectively. As illustrated in the reflective display in Figure 21B, the ionogel coupled with the Cu-Ni conductive textile is entirely flexible in all directions, enabled flexing and twisting motions without affecting the colour switching process.

While in Figure 22B, transmissive displays with cold and hot icons have also been realized with ITO/PET substrates, where they were colour switched at -20 and 100 °C, respectively. These displays have also been tested over sequential bending (radius of curvature: 2.5 cm) and flattening over 500 cycles at room temperature, showing retention of *ca.* 81% of the initial contrast at 660 nm (Figure 23).

Example 15: Crosslink Density of Composite Materials

Crosslink density of the composite materials in moles/gram have been calculated by determining the number of moles of crosslinker and dividing by mass of the composite material. Alternatively, crosslink density of the composite materials (mol/cm³) may also be determined by number of moles of crosslinker and dividing it by volume of the composite material. The crosslink density calculated for the composite material is 0.035 mol/g or 0.045 to 0.05 mol/cm³.

Comparative Example 1: Performance of Composite Materials

For comparison, the inventors evaluated and summarized the performance of various composite materials used in electrochromic applications and compare it with the present composite material and tabulated the results in Table 3.

ΔT refers to the magnitude of colour contrast or difference at a specific wavelength when the materials undergo a colour change. ΔT Endurance is a measure of the material's ability to maintain its performance without degradation after undergoing repeated testing cycles. It is typically expressed as a percentage, with 100% indicating no degradation. The parameter t_c/t_b represents the speed at which the colour switching of the materials occurs, where a smaller value indicates a faster colour-switching capability.

Table 3. Performance of composite materials used in electrochromic applications

Composite Material	Ionic Liquid	T _g (°C)	Ionic conductivity	Electrolyte preparation	ΔT (%)	t _c /t _b (s)	ΔT endurance
PEDOT/ P[ViEtIm][Br]	BMIMBr	-	0.1 mS/cm	Blend and cast vacuum dried (16 hours)	-	-	-
PEDOT/ P(VEIMBF ₄)	BMIMBF ₄	-	-	vacuum dried @ 40 °C overnight	44	2.7/3.8	-
Viologen/ P(MMA- VAc)/PMVIm- TFSI)	LiTFSI	100- 110	0.47 mS/cm (30 °C)	Blend and cast vacuum dried @ 75 °C	-	0.1	-
Viologen/ PMMEIm- TFSI P(MMA-Vac)	LiTFSI	21	0.18 mS/cm	Blend and cast vacuum dried (48 hrs)	-	0.1	-
Conjugating polymer/ P(EGDA- epoxy)	EMIMTFSI	-	-	Slot-die coated, and UV-cured (inert condition)	35	25	40% (1040 cycles)
PEDOT/ P(ILM)TFSI	LiTFSI	- 17.5	0.01 mS/cm	Blend and cast vacuum dried (2 hours)	22	3	99% (1000 cycles)
PEDOT/ PILM-TFSI	LiCl	-	10 mS/cm (RT)	Blend and cast vacuum dried @80 °C (2 hours)	28.5	3-5	99% (1000 cycles)
PEDOT-PSS/ PIL-PEG	LiTFSI	-22	0.12 mS/cm (30 °C)	Blend and spin coat vacuum dried @80 °C (4hours)	18	4.75/11.8	-
Viologen PVDF-HFP POEL-IBF ₄	TBABF ₄	-	9.84 mS/cm	Electrospinning and soaked in electrolyte	71.7	2.6/74.3	91.4% (1000 cycles)
Fe-CP/ P(BVIM TFSI)- PEGDA and P-WO ₃ / P(BVIM TFSI- LiMA)- PEGDA- (Composite materials of the present invention)	EMIMTFSI	-67.8 or - 74.7	2.67 mS/cm (20 °C)	Blend and cast Photocured (ambient condition)	45.2 and 56.4	1.9/1.5 and 1.7/6.4	94.6% (3000 cycles) and 84.3% (5000 cycles)

It is conspicuous that the composite materials prepared in this work (as described in the last row of Table 3) delivers best performance as a whole in terms of optical modulation, switching speed as well as switching stability, making them viable to be used in a variety of electrochromic applications.

As described above, benefitting from the properties of the composite materials, two high-performance ECDs have been assembled, with iron-centered coordination polymer (FeCP) and tungsten oxide (P-WO₃) electrochromic materials, achieving high colour contrast (45.2 and 56.4%), fast response time (1.5/1.9 s and 1.7/6.4 s) and good switching endurance (over thousands of switching cycles). The prepared devices (i.e. P-WO₃ device) has also been used to demonstrate thermal robustness of the ionogel, in which it could operate over a wide temperature range from -20 to 100 °C. With the use of deformable substrates (e.g., ultra-thin ITO glass, Ni-Cu conductive textile and ITO-PET), a curved electrochromic eye protector and flexible electrochromic displays were realized, suggestive of their potential in futuristic wearables.

Comparative Example 2: Comparison of Composite Materials

Table 4. Comparison of composite materials

Composition	CM A: EMIMTFSI; BVIMTFSI; PEGDA-700 CM B: EMIMTFSI; BVIMTFSI; PEGDA-700; lithium methacrylate trifluoroborate complex in propylene carbonate	Comparative Example 2a: [C ₄ mim][NTf ₂] and PPO of isocyanate crosslinker. Comparative Example 2b: and [C ₄ Dmim][NTf ₂] and PPO of isocyanate crosslinker
Polymer host / matrix	Crosslinked poly(ionic liquid)s	Crosslinked poly(urethane)
Preparation	One step photopolymerization	Thermal curing at 30-50 °C with drying agent (silica gel, calcium chloride, calcium sulphate, etc)
Time of preparation	About 1 minute	More than 24 hours
Need of co-solvent	No	Yes (organic solvent like acetone, cyclohexanone, butanone or methyl ether ketone is added for processability, which is vacuum removed after the curing

Volume reduction	No	Yes, after removal of co-solvent
Suitability for industrial coating process?	Yes Low viscosity precursor is used to form the composite materials.	No Pre-made composite materials are used which is highly viscous and not processable.
Optical changes	Transparent to transmissive coloured state (allowing partial visualization)	Transparent to opaque (block out all the view)
Mechanism	Changes in oxidation state, the role of CM A & B is to provide essential ions to counter-balance the redox changes	Lower critical solution temperature (LCST) phase separation occur to which undergo reversible microphase separation take place with temperature.
Phase separation (visual check)	No phase separation (Homogenous matrix) observed up to 100 °C	Yes phase separation observed depending on the alkyl side chain (can range from 60 °C -100 °C)
Environmental influence	Minimal/negligible. Good controllability	Phase separate once surrounding temperature rise above critical LCST. Poor controllability
Electrochemical stability	Up to +/-2.5 V	-

* C4mim refers to 1-n-butyl-3-methylimidazolium cation; C4Dmim refers to 1-butyl-2,3-dimethylimidazolium cation; and NTf2 refers to bis(trifluoromethane)sulfonimide, bis(trifluoromethanesulfonyl) amide.

The inventors have compared the composite material of the present invention with a binary ionic liquid mixture consisting of [C4mim][NTf2] and [CD4mim][NTf2] and polypropylene oxide (PPO) of isocyanate crosslinker. The isocyanate acts as a crosslinker to have the PPO form a part of a polyurethane (PU) polymer matrix.

As shown in Table 4, the polymer host/matrix in CM A and CM B of the present invention is crosslinked poly(ionic liquid)s while Comparative Examples 2a and 2b use crosslinked poly(urethane). As a result, CM A and CM B of the present invention possess low viscosity compared to other composite materials. This is because [Comparative Examples 2a and 2b are made using a polymer blend (e.g. poly(urethane) which has high viscosity. The disadvantage of a high viscosity composition is that viscosity can hinder the coating process and lead to uneven coating, resulting in defective interfaces. High viscosity of the composition would also impede its flow and uniform distribution during the coating application. This uneven distribution can negatively impact the quality of the interfaces between different layers or surfaces, affecting the overall performance and integrity of the final product. Conversely, the polymer matrix of the composite material of the present invention has low viscosity and can be applied in a controlled manner with lower viscosity, leading to improved handling and more uniform coatings. This ensures

better interface quality and reduces the likelihood of defects of the electrochromic devices. The low viscosity may be achieved by obtaining the polymer matrix via reaction of alkene groups on ionic liquid A with acrylate groups of a crosslinking agent instead of using a polymer blend. Furthermore, due to the low viscosity of the composite material, it is highly suitable for industrial coating processes while pre-made composite materials are viscous and not suited for industrial coating processes.

Furthermore, as discussed in Examples 1-3, the preparation of CM A and CM B of the present invention is simple and involves a short one-minute one-step photopolymerization while for Comparative Examples 2a and 2b, a complicated thermal curing and drying with more than 24 hours and with the need of a co-solvent is required.

Also as shown in Table 4, CM A and CM B of the present invention remains miscible (no phase separation) even if temperature is increased. However, phase separation is observed for Comparative Examples 2a and 2b. In the present invention, changes in chemical oxidation states of the composite material is the foundation of colour changes. A key distinguishing feature of the composite materials of the present invention is its temperature independence. The composite materials of the present invention remains stable and does not experience phase separation or aggregation. This remarkable feature may be attributed to the presence of electrostatic interactions between the mobile ionic liquids and the polymer matrix. These interactions stabilize the system and prevent phase separation or aggregation at different temperatures.

As shown in Example 20 and Table 4, it is observed that the composite materials of the present invention are able to change colour (bleached to colour and vice versa) and/or change in state from transparent to transmissive coloured state (allowing partial visualization) when a potential/current is applied to the composite material. However, composite materials of Comparative Examples 2a and 2b, the composite materials are only able to change its state from transparent to opaque (which blocks out all the light and visualization). With these properties, composite materials (CM A and CM B) of the present invention may be used in various applications such as in optoelectronics, electronic billboards, mirrors and displays, smart glass, wearable and portable electronics, energy-storage devices, light-emitting electrochemical cells, and many others. Composite materials (CM A and CM B) of the present invention are superior in terms of colour-changing properties, physical state and form, and applicability in comparison to composite materials of Comparative Examples 2a and 2b.

Further, it is observed that the composite materials of the present invention are able to change colour (bleached to colour and vice versa) and/or change in state from transparent to transmissive coloured state (allowing partial visualization) when a potential/current or change in temperature is applied to the composite material. However, composite materials of Comparative Examples 2a and 2b are only able to

change their state from transparent to opaque, which blocks out all the light and visualization. With these properties, composite materials (CM A and CM B) of the present invention may be used in various applications such as in optoelectronics, electronic billboards, mirrors and displays, smart glass, wearable and portable electronics, energy-storage devices, light-emitting electrochemical cells, and many others. Composite materials (CM A and CM B) of the present invention are superior in terms of colour-changing properties, physical state and form, and applicability in comparison to composite materials of Comparative Examples 2a and 2b.

Industrial Applicability

Thus, it can be seen from the present disclosure that a composite material and a method of forming the composite material has been disclosed. The composite materials are in a solid state, non-volatile, do not leak and/or seep, flexible and/or deformable with very low glass transition temperature (T_g). Hence, the composite materials are very stable with long lifetime, durable and does not pose any safety concerns. Further, the disclosed composite materials are highly transparent in visible and part of near-infrared region and thereby enables the composite material to be used for various applications such as electrochromic devices. Also, the composite materials possess excellent physicochemical stability, including thermal stability, electrochemical stability, and air stability, exhibit high ionic conductivity and possess good electrochromic performance (in terms of optical modulation, response time, stability). Hence, the composite materials may be utilized as solid-state electrolytes for electrochromic applications due to its high ionic conductivity with promising thermal and electrochemical stability. The disclosed method enables the preparation of composite materials in less than a minute under ambient conditions. The disclosed method is fast, simple and easy to perform. Furthermore, the materials required for the method is cheap and easy to obtain.

The present disclosure further discloses an electrochromic device comprising the composite material and a method of forming the electrochromic device. Benefitting from the properties of the composite material, the assembled electrochromic devices may display high colour contrast and fast response time with good endurance and exhibit great performance as an electrochromic device. The electrochromic devices show good compatibility when coupled with deformable substrates (like ultra-thin ITO glass, conductive textile, and ITO-PET substrate), to form and realize electrochromic devices such as flexible electrochromic eye protector and display applications. The disclosed method to form an electrochromic device is a rapid in-situ polymerization method, which is performed under ambient conditions. The disclosed method is simple, convenient, easy to perform and apply and require less energy demand. Furthermore, it enables easy upscaling. The disclosed in-situ method is an effective approach to improve the processability and enhance electrolyte

contact, while maintaining the dimension of the composite materials (spontaneously processed into desired geometry) in the electrochromic devices, which in turn give excellent electrochromic performance.

It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

Claims

1. An electrochromic device comprising an electrolyte sandwiched between two electrodes, the electrolyte comprising a composite material comprising:
 - an ionic liquid A, wherein the ionic liquid A is 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (EMIMTFSI); and
 - a polymer matrix comprising a network of crosslinked poly(ionic liquid B), wherein the polymer matrix is formed by reaction of an ionic liquid B with a crosslinking agent, wherein the ionic liquid B is 1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl) imide (BVIMTFSI), and the crosslinking agent is poly(ethylene glycol) diacrylate (PEGDA).
2. The electrochromic device of claim 1, wherein the polymer matrix is formed by reaction of an alkene of ionic liquid B with an acrylate of the crosslinking agent.
3. The electrochromic device of claim 1 or 2, further comprising a metal borate complex.
4. The electrochromic device of claim 3, wherein
 - the metal borate complex is lithium methacrylate trifluoroborate complex in propylene carbonate.
5. The electrochromic device of any one of claims 1 to 4, wherein the composite material is an ionogel.
6. The electrochromic device of any one of claims 1 to 5, wherein the composite material has a transmittance of about 90% to about 98% at 1 mm thickness.
7. The electrochromic device of any one of claims 1 to 6, where the composite material has a crosslink density of about 0.02 mol/g to about 0.05 mol/g, or 0.035 mol/cm³ to about 0.06 mol/cm³.
8. A method of forming an electrochromic device comprising:
 - (i) applying a mixture of ionic liquid A, ionic liquid B, crosslinking agent, a photoinitiator, and optionally a metal borate complex between two electrodes; and
 - (ii) curing the mixture with light irradiation,
 wherein the crosslinking agent reacts with ionic liquid B to form a polymer matrix comprising a network of crosslinked poly(ionic liquid B); and

 wherein the ionic liquid A is 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (EMIMTFSI), the ionic liquid B is 1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl) imide (BVIMTFSI), and the crosslinking agent is poly(ethylene glycol) diacrylate (PEGDA).

9. The method of claim 8, wherein step (ii) is performed for a duration of about 30 seconds to about 90 seconds.
10. The method of claim 8 or 9, wherein the photoinitiator is selected from the group consisting of diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO), benzophenone, phenyl bis (2,4,6-trimethylbenzoyl)phosphine oxide, 2-hydroxy-2-methyl-1-phenyl-propan-1-one, 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone, 2,2'-azobis[2-methyl-n-(2-hydroxyethyl)propionamide], 2,2-dimethoxy-2-phenylacetophenone, lithium phenyl(2,4,6-trimethylbenzoyl)phosphinate), and ethyl (2,4,6-trimethylbenzoyl) phenylphosphinate.
11. Use of a composite material as an electrolyte sandwiched between two electrodes in an electrochromic device, the composite material comprising:
 - an ionic liquid A, wherein the ionic liquid A is 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (EMIMTFSI); and
 - a polymer matrix comprising a network of crosslinked poly(ionic liquid B), wherein the polymer matrix is formed by reaction of an ionic liquid B with a crosslinking agent, wherein the ionic liquid B is 1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl) imide (BVIMTFSI), and the crosslinking agent is poly(ethylene glycol) diacrylate (PEGDA).
12. The use of claim 11, wherein the polymer matrix is formed by reaction of an alkene of ionic liquid B with an acrylate of the crosslinking agent.
13. The use of claim 11 or 12, further comprising a metal borate complex.
14. The use of claim 13, wherein the metal borate complex is lithium methacrylate trifluoroborate complex in propylene carbonate.
15. The use of any one of claims 11 to 14, wherein the composite material is an ionogel.
16. The use of any one of claims 11 to 15, wherein the composite material has a transmittance of about 90% to about 98% at 1 mm thickness.
17. The use of any one of claims 11 to 16, where the composite material has a crosslink density of about 0.02 mol/g to about 0.05 mol/g, or 0.035 mol/cm³ to about 0.06 mol/cm³.