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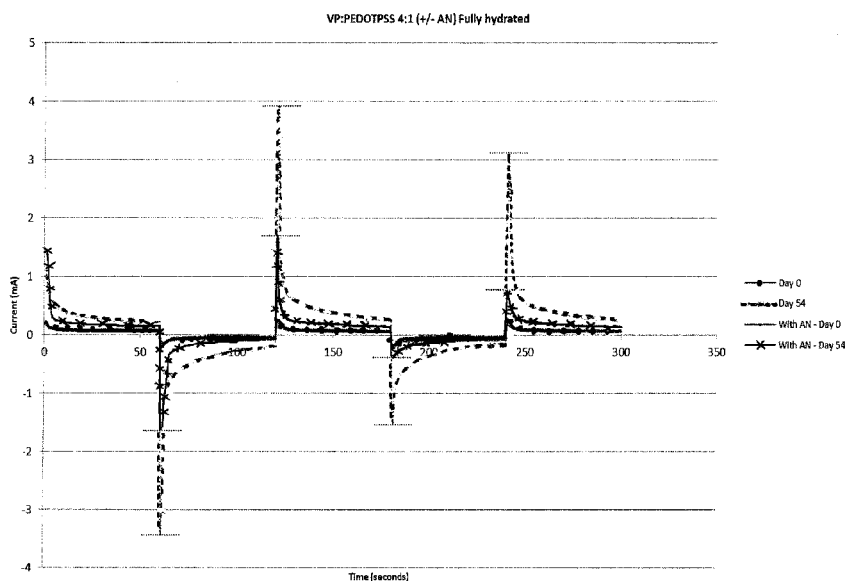


Figure 1 VP-PEDOTPSS 4:1 (with and without AN) after a maximum level of hydration was achieved

(57) Abstract: A process of forming a cross-linked electronically active hydrophilic co-polymer comprising the steps of: a. mixing an intrinsically electronically active material with water to form an intermediate mixture; b. adding at least one hydrophilic monomer, at least one hydrophobic monomer, and at least one cross-linker to the intermediate mixture to form a co-monomer mixture; c. polymerising the co-monomer mixture.

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Electrically conducting hydrophilic co-polymers

Field of the invention

The present invention relates to electronically active hydrophilic polymers
5 and their production.

Background of the invention

Intrinsically electronically conductive polymers are known, and are
understood to mean materials in which the conduction process is principally
dependent upon electron transfer. This is in contrast to ionically conductive
10 polymers, where the conduction process is principally dependent on ion transfer.

As a result of their electronic conductivity, electronically conductive
polymers may have applicability within electronic systems, such as car batteries,
mobile phone screens and computer screens. The functioning of these
electronic systems relies on the transmission and proper control of electrons.
15 Electronically conductive polymers include polyacetylene, which has achieved
electrical conductivities of 10^7 S/m approximating to that of common metals,
while commercial materials supplied as dispersions in water, e.g.
polyethylenedioxythiophene:polystyrene sulphonate (PEDOT:PSS, commercially
available as Clevios 500®), have a conductivity of 3×10^4 S/m and exceed the
20 conductivity of graphite commonly used as a conductor in electrochemical cells.

However, electronically conductive polymers have poor water properties,
and this limits their applicability in aqueous environments. These electronically
conductive polymers become unstable when dispersed or dissolved in aqueous
environments. They are therefore of most use when they are dry, and are of very
25 limited use in electronic systems with a water-based environment e.g. car
batteries. Water-based environments in electronic systems may be saline, acid
or alkaline aqueous environments.

Further, electronically conductive polymers can be challenging to
produce, and are usually produced as a non-self-supporting film. Owing to their
30 non-self-supporting nature, polymerisation is carried out on a solid support, such
as a glass sheet, in order to form these polymers. As such, the resulting
polymer is a largely two-dimensional film, rather than a bulk three-dimensional
structure.

Summary of the invention

It has been found that, when mixed in a particular order, a co-monomer mixture comprising at least one hydrophobic monomer, at least one hydrophilic monomer, water, at least one cross-linker, and an intrinsically electronically active material, provides (once polymerised) a new electronically active hydrophilic co-polymer. This material is homogenous and isotropic in its conductive properties, and in its water properties. It is hydrophilic, crosslinked and electronically conductive, throughout its entire structure.

As a result of their hydrophilicity, the co-polymers described herein have good water properties resulting in improved performance in aqueous environments of electronic systems (existing hydrophilic materials are ionically conductive, rather than electronically conductive). The co-polymers are stable in a wide-variety of different water-based environments, and perform well not only in distilled deionized (DD) water, but also in aqueous environments such as saline, acid or alkali solution. Furthermore, the co-polymers described herein also have excellent mechanical properties and electrical conductivity. As such, the co-polymer materials disclosed herein have wide applicability within electronic systems, including those with water-based environments, such as car batteries. This is in contrast to existing electronic materials such as PEDOT:PSS, which is conventionally used only in dry environments, owing to its poor water properties.

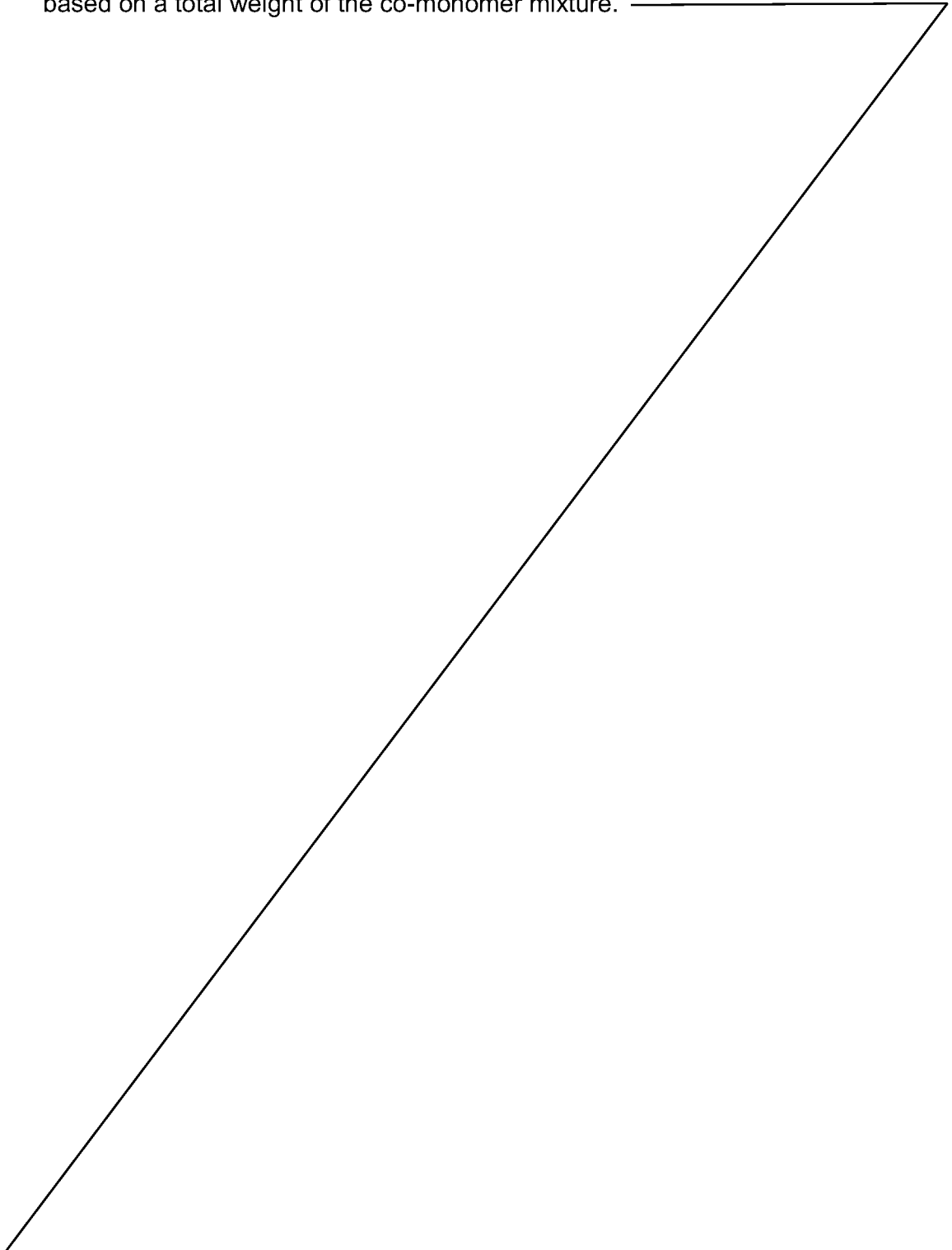
Further, the specific order of mixing used to obtain the co-monomer mixture allows a bulk three-dimensional co-polymer structure to be achieved (rather than a largely two-dimensional polymer film). The resulting co-polymer is self-supporting, and as such does not need to be polymerized onto a substrate.

In addition, it has been found that the amount of water in the co-monomer mixture must be sufficient to provide a uniformly mixed homogenous solution or dispersion, and must be sufficient to uniformly disperse the intrinsically electronically active material, which is insoluble in water. In particular, the amount of water in the co-monomer mixture may be 5% to 50% by weight.

In a first aspect the present invention provides a process of forming a cross-linked electronically active hydrophilic co-polymer comprising the steps of:

a. mixing an intrinsically electronically active material with water to form an intermediate mixture;

- b. adding at least one hydrophilic monomer, at least one hydrophobic monomer, and at least one cross-linker to the intermediate mixture to form a co-monomer mixture;
 - c. polymerising the co-monomer mixture;
- 5 wherein the amount of water in the co-monomer mixture is 5% - 50% by weight, based on a total weight of the co-monomer mixture.



In a second aspect, the present invention provides a homogenous, isotropic electronically active hydrophilic co-polymer obtainable by the process according to the first aspect of the invention.

5 In a third aspect, the present invention provides a co-monomer mixture comprising at least one hydrophobic monomer, at least one hydrophilic monomer, water, at least one cross-linker, and an intrinsically electronically active material.

Further aspects are defined in the independent claims and include a variety of industrial products that make use of electronic systems. One such industrial product is a supercapacitor. As a result of their improved electronic properties, the co-polymers described herein may be used as the electrolyte component within a supercapacitor system. When the co-polymers described herein are used in this context, the resulting supercapacitor achieves particularly high capacitance values. Furthermore, as a result of the improved mechanical properties and self-supporting nature of the co-polymers described herein, the resulting supercapacitor does not require an additional separator.

Description of the preferred embodiments

As used herein, the term “monomer” takes its usual definition in the art, and so refers to a molecular compound that may chemically bind to another monomer to form a polymer.

As used herein, the term “co-monomer mixture”, takes its usual definition in the art, and so refers to a solution or dispersion of miscible monomers that, when polymerised, forms a co-polymer.

25 As used herein, the term “cross-linker” refers to molecular compound capable of forming chemical bonds between polymer chains, and includes compounds such as methylenebisacrylamide, N-(1-Hydroxy-2,2-dimethoxyethyl)acrylamide, allyl methacrylate and ethylene glycol dimethacrylate. Allyl methacrylate and ethylene glycol dimethacrylate are preferred. The cross-linker may be hydrophobic or hydrophilic.

As used herein, the term “polymerisation initiator” takes its usual definition in the art, and so refers to an agent capable of initiating the process of chemical polymerisation, for example free-radical polymerisation. Azobisisobutyronitrile (AIBN) and-hydroxy-2-methylprophenone are examples of

such initiators. Azobisisobutyronitrile (AIBN) has utility when polymerisation is by thermal means, and 2-hydroxy-2-methylpropiophenone is suitable for use with UV polymerisation.

As used herein, the term “intermediate mixture” refers to a solution or dispersion to which further components are added. For instance, in the context of forming the co-monomer mixture, the term “intermediate mixture” refers to a mixture including some, but not all the components of the complete co-monomer mixture.

As used herein, the term “co-polymer” takes its usual definition in the art, and so refers to a polymer whose polymer chains comprise two or more different types of monomers.

As used herein, the term “water properties” when used in relation to a polymer material, refers the properties and behaviour of that polymer material in relation to water and other aqueous environments, such as saline solution i.e. its hydrophilicity and stability in an aqueous environment.

As used herein, the term “homogenous”, when used in relation to a polymer material, refers to a polymer material whose physical properties (e.g. conductive properties and water properties) are substantially uniform throughout its entire structure.

As used herein, the term “isotropic”, when used in relation to a polymer material, refers to a polymer material whose properties are the same in all orientations.

As used herein, the term “homogenous” when used in relation to a co-monomer mixture, refers to a co-monomer solution or dispersion comprising miscible monomers that are uniformly dissolved or mixed.

As used herein, the term “hydrophilic polymer” refers to a polymer that dissolves in water when it is not cross-linked and absorbs water and swells to form a stable elastic solid when cross-linked.

As used herein, the term “hydrophilic monomer” takes its usual definition in the art, and so refers to a monomer with an affinity for water molecules. The term “hydrophobic monomer” also takes its usual definition in the art, and so refers to a monomer that repels water molecules.

As used herein, the term “electrically active” takes its usual definition in the art, and so can encompass both electronically active and ionically active materials.

As used herein, the term “electronically active material” takes its usual definition in the art, and refers to a material in which the conduction process is principally dependent upon electron transfer, or in which an electron is yielded as an output at an interface.

As used herein, the term “intrinsically electronically active material” refers to a material that is electronically active without requiring further modification to be rendered electronically active.

As used herein, the term “ionically active material” takes its usual definition in the art, and refers to a material in which the conduction process is principally dependent on ion transfer.

As used herein, the term “water” as a component in the intermediate or co-monomer mixture refers to added water, i.e. water added to the remaining components not including any water already associated with the raw materials of the remaining components, e.g. when such raw materials are supplied as an aqueous solution or dispersion.

As used herein, the term “liquid electrolyte” takes its usual definition in the art, and so refers to a solution of cations (such as potassium, sodium, calcium and magnesium) and anions (such as chloride, carbonate and phosphate) dissolved in a solvent, such as water, acetonitrile, propylene carbonate or tetrahydrofuran. As used herein, the term “aqueous electrolyte” takes its usual definition in the art, and so refers to an aqueous solution containing cations (such as potassium, sodium, calcium and magnesium) and anions (such as chloride, carbonate and phosphate).

As used herein, the term “optoelectronic display device” takes its usual definition in the art, and so refers to a device capable of sourcing, detecting and controlling electromagnetic energy, such as infra-red ultraviolet, or visible light.

In a first aspect the present invention provides a process of forming a cross-linked electronically active hydrophilic co-polymer comprising the steps of:

- a. mixing an intrinsically electronically active material with water to form an intermediate mixture;

- b. adding at least one hydrophilic monomer, at least one hydrophobic monomer, and at least one cross-linker to the intermediate mixture to form a co-monomer mixture;
- c. polymerising the co-monomer mixture.

5 Preferably, the electronically active material is a polymer

It has been found that when the components are mixed in the specific order according to the first aspect of the present invention, a homogenous co-monomer mixture is obtained. This is in contrast to the other possible orders of mixing, where the components are prone to separate out into distinct layers during the polymerisation process, thereby preventing the formation of a continuous material. As these problems are avoided with the process disclosed
10 herein, a continuous bulk three-dimensional co-polymer structure is achieved, that is of a self-supporting nature.

Preferably, the intrinsically electronically active material is PEDOT:PSS.
15 The problems associated with other orders of mixing aside from that of the process disclosed herein are particularly pronounced for PEDOT:PSS. Yet, when PEDOT:PSS is used as the intrinsically electronically active material in the context of the present invention, good results are achieved, as shown in the examples.

20 Preferably, in step b, the at least one hydrophilic monomer and the at least one hydrophobic monomer are added to the intermediate mixture prior to the addition of the cross-linker.

Preferably, in step b, the at least one hydrophilic monomer is added to the intermediate mixture prior to the addition of the at least one hydrophobic
25 monomer.

Preferably, the at least one hydrophilic monomer is selected from methacrylic acid, hydroxyethyl methacrylate (e.g. 2-hydroxyethyl methacrylate), ethyl acrylate, vinyl pyrrolidone (e.g. n-vinyl-2-pyrrolidone), propenoic acid methyl ester (e.g. propenoic acid 2-methyl ester), monomethacryloyloxyethyl
30 phthalate, poly-vinyl alcohol, ammonium sulphatoethyl methacrylate, or a combination thereof. Preferably, the co-monomer mixture comprises one hydrophilic monomer.

More preferably, the at least one hydrophilic monomer is selected from vinyl-2-pyrrolidone (VP) and 2-hydroxyethyl methacrylate, or a combination

thereof. More preferably, the at least one hydrophilic monomer is selected from 1-vinyl-2-pyrrolidone (VP) and 2-hydroxyethyl methacrylate, or a combination thereof.

5 Preferably, the at least one hydrophobic monomer is selected from methyl methacrylate, acrylonitrile (AN), methacryloxypropyltris(trimethylsiloxy)silane, 2,2,2-trifluoroethyl methacrylate, allyl methacrylate, or a combination thereof. Preferably, the co-monomer mixture comprises one hydrophobic monomer.

10 More preferably, the at least one hydrophobic monomer is selected from acrylonitrile and methyl methacrylate, or a combination thereof.

Preferably, the at least one cross-linker is selected from allyl methacrylate or ethylene glycol dimethacrylate.

15 It will be appreciated from the definitions above, that the terms used above are not necessarily mutually exclusive. For example, the terms “hydrophobic monomer” and “cross-linker” are not necessarily mutually exclusive. In the present invention, the hydrophobic monomer and the cross-linker may be the same or different.

20 The hydrophobic monomer may, in certain embodiments, be the same as the cross-linker. For example, in certain embodiments, both the cross-linker and the hydrophobic monomer are allyl methacrylate.

25 In some embodiments, the hydrophilic monomer and/or the hydrophobic monomer are non-cross-linking. There is no overlap between the terms “non-cross-linking hydrophobic monomer”, “non-cross-linking hydrophilic monomer” and “cross-linker”. In these embodiments, the cross-linker, the hydrophobic monomer and the hydrophilic monomers are different chemical species.

Preferably, the hydrophobic monomer is a different chemical species to the cross-linker. In these embodiments, the use of a hydrophobic monomer that is different to the cross-linker allows the formation of a co-polymer with particularly good mechanical stability, as stated in the Examples.

30 Preferably, the polymerisation step is carried out by thermal, UV or gamma radiation.

More preferably, the polymerisation step is carried out by UV or gamma radiation.

In a preferred embodiment, the co-monomer mixture further comprises a polymerisation initiator. The polymerisation initiator may be azobisisobutyronitrile (AIBN) or 2-hydroxy-2-methylpropiophenone.

5 The presence of a polymerisation initiator is particularly preferred when the polymerisation is by thermal or UV radiation. In one embodiment, the polymerisation is by thermal means and the initiator is azobisisobutyronitrile (AIBN). In another embodiment, the polymerisation is by UV radiation and the initiator is 2-hydroxy-2-methylpropiophenone.

10 The individual components of the co-monomer mixture should be included in sufficient quantities such that they mix uniformly thereby forming a homogenous solution or dispersion.

The hydrophobic monomer may be present in an amount of 5% to 80% by weight, preferably, 5% to 60% by weight, most preferably 5% to 20% by weight based on the total weight of the co-monomer mixture. The hydrophilic
15 monomer may be present in an amount of 5% to 90% by weight, preferably 5% to 80% by weight, most preferably 50% to 70% by weight based on the total weight of the co-monomer mixture. The cross-linker agent may be present in the co-monomer mixture in an amount of 1% to 25% by weight, preferably 2% to 15% by weight, most preferably 2% to 10% by weight based on the total weight
20 of the co-monomer mixture. The intrinsically electronically active material may be present in an amount of 1% to 20% by weight and most preferably 2% to 10% by weight.

The amount of water in the co-monomer mixture must be sufficient to provide a uniformly mixed homogenous solution or dispersion, and must be
25 sufficient to uniformly disperse the intrinsically electronically active material, which is insoluble in water. The amount of water in the co-monomer mixture may be 5% to 50% by weight, preferably 5% to 20% by weight based on the total weight of the co-monomer mixture.

30 Preferably, the ratio of the at least one hydrophilic monomer to the at least one hydrophobic monomer is from 20:1 to 1:1, more preferably, 20:1 to 5:1, in particular 10:1, in the co-monomer mixture.

Preferably, the ratio of the at least one hydrophilic monomer and the at least one hydrophobic monomer : the intrinsically electronically active material is from 30:1 to 2:1, more preferably 6:1 to 3:1, in the co-monomer mixture.

Preferably, the ratio of the water to the intrinsically electronically active material is from 1:1 to 10:1, preferably 1:1 to 3:1, in particular 2:1, in the co-monomer mixture.

5 It has been found that particularly good results are achieved when using the components in the preferable ratios set out above. When used in these ratios, the components are particularly miscible with each other, and this assists the polymerisation process and the formation of a continuous bulk co-polymer material. The ratios referred to are the volume ratios of the various components.

10 In a preferred embodiment, the co-polymer is hydrated following polymerisation. This hydration step may be carried out using distilled deionized (DD) water, or with an aqueous solution, such as saline, brine, acid, or alkali solution. When saline solution is used for the hydration step, the saline solution preferably has 0.002 g/cc to 0.1 g/cc of NaCl in water, more preferably 0.009 g/cc of NaCl in water. When brine solution is used for the hydration step, the
15 brine solution preferably has 0.3 g/cc of NaCl in water. When acid solution is used for the hydration step, the acid is preferably 5mol/dm^3 H_2SO_4 . When alkali solution is used for the hydration step, the alkali solution is preferably an aqueous solution of KOH with the KOH is present at 10 wt% to 30 wt%. It is preferred that this hydration step results in the amount of water in the co-polymer being at least 10% by weight, preferably at least 20% by weight, based on the
20 total weight of the hydrated co-polymer. Without wishing to be bound by theory, when water is present in this quantity, then it can act as a "plasticizer" and enable the other components of the co-polymer to have sufficient intermolecular mobility such that the conformation of the co-monomer self-organises over time.
25 For example, this self-organisation can occur within a period of about 7-14 days. It has been observed that, following manufacture and/or further hydration, the electrical properties of the co-polymer improve over time. As such, in a preferred embodiment, the co-polymer is stored for at least 7 days, preferably for at least 14 days, following hydration. Not only are the co-polymers stable
30 following hydration, but they also display improved electrical conductivity, as will be shown in the examples, where the properties are demonstrated to improve over a period of 54 days after hydration.

The co-monomer mixture may be provided and polymerised using UV, gamma or thermal radiation. The UV or gamma radiation may be carried out

under ambient temperature and pressure, whilst thermal polymerisation may be carried out at temperatures up to 70 °C.

In a second aspect the present invention provides a homogenous and isotropic electronically active hydrophilic co-polymer obtainable by the process according to any of the embodiments set out with respect to the first aspect of the invention. It is believed that such a homogeneous co-polymer is novel.

In a third aspect, the present invention provides a co-monomer mixture comprising at least one hydrophobic monomer, at least one hydrophilic monomer, water, at least one cross-linker, and an intrinsically electronically active material.

Preferred hydrophobic monomers, hydrophilic monomers, intrinsically electronically active materials and cross-linkers are defined above.

The polymerisation of the above-mentioned co-monomer mixtures result in the homogenous, isotropic electronically active hydrophilic co-polymers disclosed herein.

Co-polymers and co-monomer mixtures disclosed herein can be used in a variety of applications, and are particularly useful in electronic systems with a water-based environment. However, the co-polymers disclosed herein also provide benefits when used in other electronic systems i.e. those with non-water-based environments, owing to their excellent mechanical properties and electrical conductivity.

Preferably, the co-monomer mixture disclosed herein is used in 3D printing, wherein the co-monomer mixture is polymerised to form a 3D image. It is thought that the hydrophilicity of the co-polymers formed from the co-monomer mixture is advantageous when forming a 3D printed image.

Preferably, the co-polymers disclosed herein are used in a battery together with an aqueous electrolyte. Preferably, the battery is a lead acid battery. Alternatively, the co-polymers disclosed herein are used in an electrochemical cell together with water or an aqueous electrolyte. In this embodiment, the battery or electrochemical cell may be flexible, which is possible due to the advantageous properties of the co-polymers of the present invention. In certain embodiments, the co-polymers disclosed herein are used in a photovoltaic cell.

Preferably, the co-polymers disclosed herein are used as the electrolyte component within a supercapacitor system. As will be appreciated by the skilled person, supercapacitors generally comprise two electrodes and an electrolyte component located therebetween. The maximum capacitance value achieved by a supercapacitor may depend on the nature of the electrolyte as well as the nature of the electrodes. As will also be appreciated by the skilled person, there are multiple different kinds of supercapacitor systems. These include double-layer supercapacitors, pseudo-capacitive supercapacitors, and hybrid supercapacitors. Double-layer supercapacitors typically comprise carbon electrodes that are of comparatively low cost. The capacitance of double-layer supercapacitors is largely electrostatic capacitance. Meanwhile, pseudo-capacitive supercapacitors comprise comparatively higher cost electrodes that are capable of undergoing an oxidation-reduction (redox) reaction together with the electrolyte. Such redox active electrodes can comprise, for example, lanthanum ruthenium or vanadium. The capacitance of pseudo-capacitive supercapacitors is therefore significantly increased (or augmented) by electrochemical capacitance. Hybrid supercapacitors comprise a combination of electrodes with differing characteristics, and can for example comprise one carbon electrode and one electrode capable of undergoing a redox reaction with the electrolyte. The capacitance of hybrid supercapacitors is therefore a combination of electrostatic capacitance and electrochemical capacitance. Conventionally, the electrolyte component within the above supercapacitor systems is a liquid electrolyte.

When the co-polymers disclosed herein are used in place of the conventional liquid electrolyte of a supercapacitor, the resulting supercapacitor achieves particularly high capacitance values. Without wishing to be bound by theory, it is thought that pseudo-capacitive supercapacitors achieve higher capacitance values due to the ability of the electrolyte and the electrodes to undergo a redox reaction with each other. Without wishing to be bound by theory, it is thought that the electronic properties of the co-polymers disclosed herein are such that an effective redox reaction is achieved, thereby providing particularly increased capacitance values. Good capacitance values are also achieved in the context of hybrid supercapacitors. In summary, for a given supercapacitor system and with a given electrode, the maximum capacitance is increased when

using the co-polymers disclosed herein as the electrolyte component within a supercapacitor. Further, the co-polymers remain stable across a commercially acceptable voltage range.

Furthermore, as a result of the improved mechanical properties and self-supporting nature of the co-polymers described herein, a supercapacitor including the co-polymers disclosed herein as the electrolyte component does not require an additional separator. Conventionally, when a liquid electrolyte is used within a supercapacitor system, it is necessary for the supercapacitor to further comprise an additional separator in order to maintain separation between the two electrodes. When the co-polymers described herein are used in place of the conventional liquid electrolyte, their mechanical properties and self-supporting nature is such that separation between the electrodes is maintained even in absence of an additional separator.

In another embodiment, the co-polymers disclosed herein are used in a sensing system. Sensing systems may include one or more chemical components, where these chemical components are capable of detecting a particular compound. Advantageously, these one or more chemical components may be dispersed throughout the structure of the co-polymers disclosed herein, and the resulting co-polymer included in the sensing system. The co-polymers disclosed herein act as a support matrix for the chemical components, wherein the chemical components are stably retained within the co-polymer structure, and their sensing ability preserved. The particular compounds detected by such sensing systems can include glucose. The skilled person will be familiar with the chemical components capable of detecting glucose, and such chemical components can include Benedict's reagent (which comprises anhydrous sodium carbonate, sodium citrate and copper(II) sulfate pentahydrate).

In another embodiment, the co-polymers disclosed herein are used in an optoelectronic display device. In this embodiment, the optoelectronic display device is preferably flexible, which is possible due to the advantageous properties of the co-polymers of the present invention.

In another embodiment, the co-polymers disclosed herein may be used to form an electrically conducting adhesive junction, wherein the adhesive junction is positioned between adjacent electrically conducting components. Preferably,

the adjacent electrically conducting components together with the adhesive junction form a stack of integrated circuits, such as a stack of 2D electrical chips.

The present invention will now be demonstrated according to the following examples.

5

Example 1: 4:1 VP to PEDOT-PSS

A first hydrophilic co-polymer was prepared using vinyl pyrrolidone and PEDOT-PSS in a 4:1 ratio, together with allyl-methacrylate (as crosslinking agent and hydrophobic co-monomer). In addition, a second hydrophilic co-polymer was prepared using vinyl pyrrolidone and PEDOT-PSS in a 4:1 ratio, together with allyl methacrylate (as crosslinking agent) and acrylonitrile (AN) (as hydrophobic co-monomer).

To obtain a 4:1 ratio of VP to PEDOT-PSS, 1.5ml of water was added to 1ml of PEDOT-PSS whilst stirring using a magnetic stirrer bar. 4ml of 1-vinyl-2-pyrrolidone was then added dropwise to the PEDOT-PSS/water mixture. After a homogenous mixture was obtained, 0.195ml of allyl methacrylate was added, as was 0.13ml of 2-hydroxy-2-methylpropiophenone (as the initiator). The co-monomer mixture was then cured under UV to produce the first crosslinked co-polymer.

The above process was repeated with the additional step that 6 weight % of acrylonitrile was added to the co-monomer mixture following the addition of crosslinking agent (allyl methacrylate) and prior to the curing step, to obtain the second crosslinked co-polymer.

Each co-polymer was hydrated in DD water, and the conductivity tested immediately after a maximum level of hydration was achieved; for the first co-polymer (i.e. no acrylonitrile present) this was when a water content of approximately 69% was reached, and for the second co-polymer (i.e. with acrylonitrile present) this was when a water content of approximately 63% was reached. The electrical properties were then measured following a period of 54 days after hydration. The results are shown in Table 1 (below) and in Figure 1.

In Table 1, the term "expansion ratio" refers to the thickness of the co-polymer (i.e. the shortest linear dimension of the co-polymer) after a maximum level of hydration has been reached divided by the thickness of the co-polymer before hydration. The thickness was measured by any suitable means such as a micrometer, vernier callipers or a travelling microscope.

VP:PEDOTPSS + water hydrated	No. of days after initial hydration	Mass (g)	Expansion ratio	Minimum current (mA)	Maximum current (mA)
4:1	0	0.814	1.53	0.05	0.24
	54	0.810		0.20	3.90
4:1 with AN	0	0.912	1.44	0.05	0.25
	54	0.899		0.08	1.68

Table 1

As can be seen, both co-polymers display good electrical conductivity immediately after hydration. Both co-polymers displayed improved electrical properties after 54 days following hydration. The addition of acrylonitrile (AN) provides co-polymers that maintain a good level of electrical conductivity, whilst improving the mechanical properties of the polymer before and after hydration.

10 Example 2: 3:1 VP to PEDOT-PSS

A first hydrophilic co-polymer was prepared using vinyl pyrrolidone and PEDOT-PSS in a 3:1 ratio, together with allyl-methacrylate (as crosslinking agent and hydrophobic co-monomer). In addition, a second hydrophilic co-polymer was prepared using vinyl pyrrolidone and PEDOT-PSS in a 3:1 ratio, together with allyl methacrylate (as crosslinking agent) and acrylonitrile (as hydrophobic co-monomer).

Each of these co-polymers was prepared using the same method as that of Example 1, except that 3ml (rather than 4ml) of 1-vinyl-2-pyrrolidone was used.

20 Each co-polymer was hydrated in DD water, and the conductivity tested immediately after maximum level of hydration was achieved; for the first co-polymer (i.e. no acrylonitrile present) this was when a water content of approximately 61% was reached, and for the second co-polymer (i.e. with acrylonitrile present) this was when a water content of approximately 57% was reached. The electrical properties were then measured following a period of 54 days after hydration. The results are shown in Table 2 (below) and in Figure 2. The expansion ratio in Table 2 was calculated in the same manner as for Table 1.

VP:PEDOTPSS + water hydrated	No. of days after initial hydration	Mass (g)	Expansion ratio	Minimum current (mA)	Maximum current (mA)
3:1	0	0.893	1.42	0.08	0.39
	54	0.890		0.12	1.85
3:1 with AN	0	0.864	1.38	0.06	0.34
	54	0.866		0.08	1.32

Table 2

As with Example 1, both co-polymers display good electrical conductivity immediately after hydration. Both co-polymers displayed improved electrical properties after 54 days following hydration. The addition of acrylonitrile (AN) provides co-polymers that maintain a good level of electrical conductivity, whilst improving the mechanical properties of the polymer before and after hydration.

For both examples 1 and 2, hydration was required to achieve optimal electrical conductivity.

Throughout the specification and the claims that follow, unless the context requires otherwise, the words “comprise” and “include” and variations such as “comprising” and “including” will be understood to imply the inclusion of a stated integer or group of integers, but not the exclusion of any other integer or group of integers.

The claims defining the invention are as follows:

1. A process of forming a cross-linked electronically active hydrophilic copolymer comprising the steps of:

a. mixing an intrinsically electronically active material with water to form an intermediate mixture;

b. adding at least one hydrophilic monomer, at least one hydrophobic monomer, and at least one cross-linker to the intermediate mixture to form a co-monomer mixture; and

c. polymerising the co-monomer mixture;

wherein the amount of water in the co-monomer mixture is 5% - 50% by weight, based on a total weight of the co-monomer mixture.

2. The process according to claim 1, wherein, in step b, the at least one hydrophilic monomer and the at least one hydrophobic monomer are added to the intermediate mixture prior to the addition of the cross-linker.

3. The process according to claim 1 or claim 2, wherein, in step b, the at least one hydrophilic monomer is added to the intermediate mixture prior to the addition of the at least one hydrophobic monomer.

4. The process according to any one of the preceding claims, wherein the intrinsically electronically active material is selected from polyethylenedioxythiophene:polystyrene sulphonate, polypyrrole, polyaniline, polyacetylene, or a combination thereof.

5. The process according to any one of the preceding claims, wherein the at least one hydrophilic monomer is selected from methacrylic acid, 2-hydroxyethyl methacrylate, ethyl acrylate, vinyl pyrrolidone, propenoic acid methyl ester, monomethacryloyloxyethyl phthalate, ammonium sulphatoethyl methacrylate, poly vinyl alcohol or a combination thereof.

6. The process according to any one of the preceding claims, wherein the at least one hydrophobic monomer is selected from methyl methacrylate, allyl methacrylate, acrylonitrile, methacryloxypropyltris(trimethylsiloxy)silane, 2,2,2-trifluoroethyl methacrylate, or a combination thereof.

7. The process according to any one of the preceding claims, wherein the cross-linker is allyl methacrylate or ethylene glycol dimethacrylate.
8. The process according to any one of the preceding claims, wherein both the cross-linker and the hydrophobic monomer is allyl methacrylate.
9. The process according to any one of the preceding claims, wherein the polymerisation step is carried out by thermal, UV or gamma radiation.
10. The process according to any one of the preceding claims, wherein the co-monomer mixture further comprises a polymerisation initiator.
11. The process according to claim 10, wherein the polymerisation initiator is azobisisobutyronitrile or 2-hydroxy-2-methylpropiophenone.
12. The process according to any one of the preceding claims, wherein the at least one hydrophilic monomer and the at least one hydrophobic monomer are present in the co-monomer mixture at a ratio of from 20:1 to 1:1.
13. The process according to any one of the preceding claims, wherein the at least one hydrophilic monomer and the at least one hydrophobic monomer are present in the co-monomer mixture in a ratio to the intrinsically electronically active material of from 30:1 to 2:1.
14. The process according to any one of the preceding claims, wherein the water is present in the co-monomer mixture in a ratio to the intrinsically electronically active material of from 1:1 to 10:1.
15. The process according to any one of the preceding claims, further comprising the step of hydrating the co-polymer after polymerisation.
16. The process according to any one of the preceding claims, wherein the co-polymer is stored for at least 7 days following hydration.
17. The process according to claim 15 or claim 16, wherein the co-polymer is hydrated such that the hydrated co-polymer comprises at least 10 wt% water, based on the total weight of the hydrated co-polymer.

18. A homogenous, isotropic electronically active hydrophilic co-polymer obtained by the process according to any one of the preceding claims.

19. A co-monomer mixture comprising at least one hydrophobic monomer, at least one hydrophilic monomer, water, at least one cross-linker, and an intrinsically electronically active material, wherein the amount of water in the co-monomer mixture is 5% - 50% by weight, based on a total weight of the co-monomer mixture.

20. The co-monomer mixture according to claim 19, having any one of the additional features of claims 2-8 or 10-14.

21. Use of a co-monomer mixture according to claim 19 or claim 20, in 3D printing, wherein the co-monomer mixture is polymerised to form a 3D image.

22. Use according to claim 21, wherein the 3D printing uses a screen printing system or an ink-jet printing system.

23. A battery comprising an aqueous electrolyte and a co-polymer according to claim 18.

24. The battery of claim 23, wherein the battery is a lead acid battery.

25. An electrochemical cell comprising water or an aqueous electrolyte and a co-polymer according to claim 18.

26. An optoelectronic display device comprising a co-polymer according to claim 18, wherein the optoelectronic display device is flexible.

27. A mobile phone screen or a computer screen comprising a co-polymer according to claim 18.

28. A supercapacitor comprising two electrodes and a co-polymer according to claim 18 located therebetween.

29. A sensing system comprising a co-polymer according to claim 18 with a chemical component dispersed throughout its structure, wherein said chemical component is capable of detecting a particular compound.

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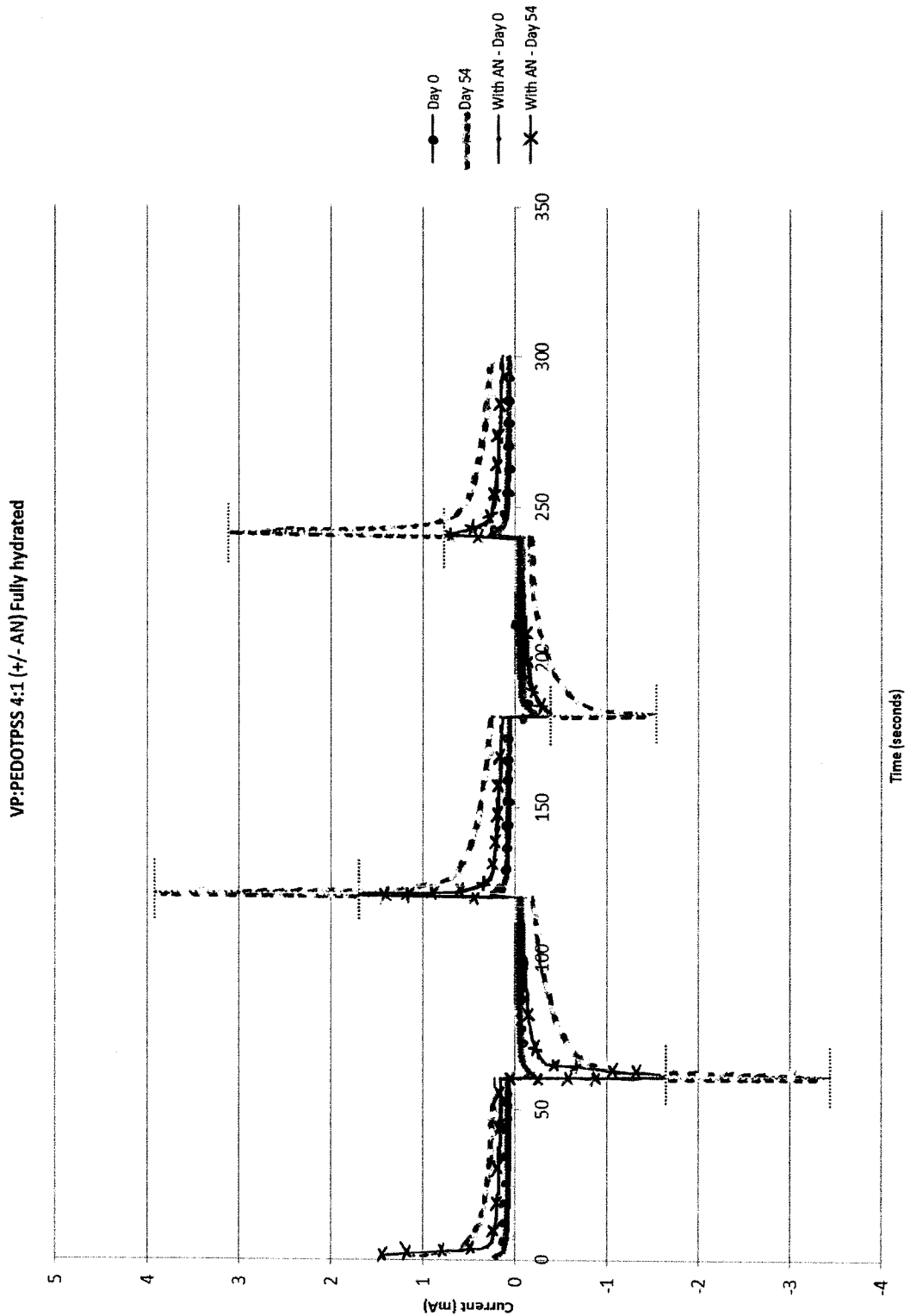


Figure 1 VP-PEDOTPSS 4:1 (with and without AN) after a maximum level of hydration was achieved

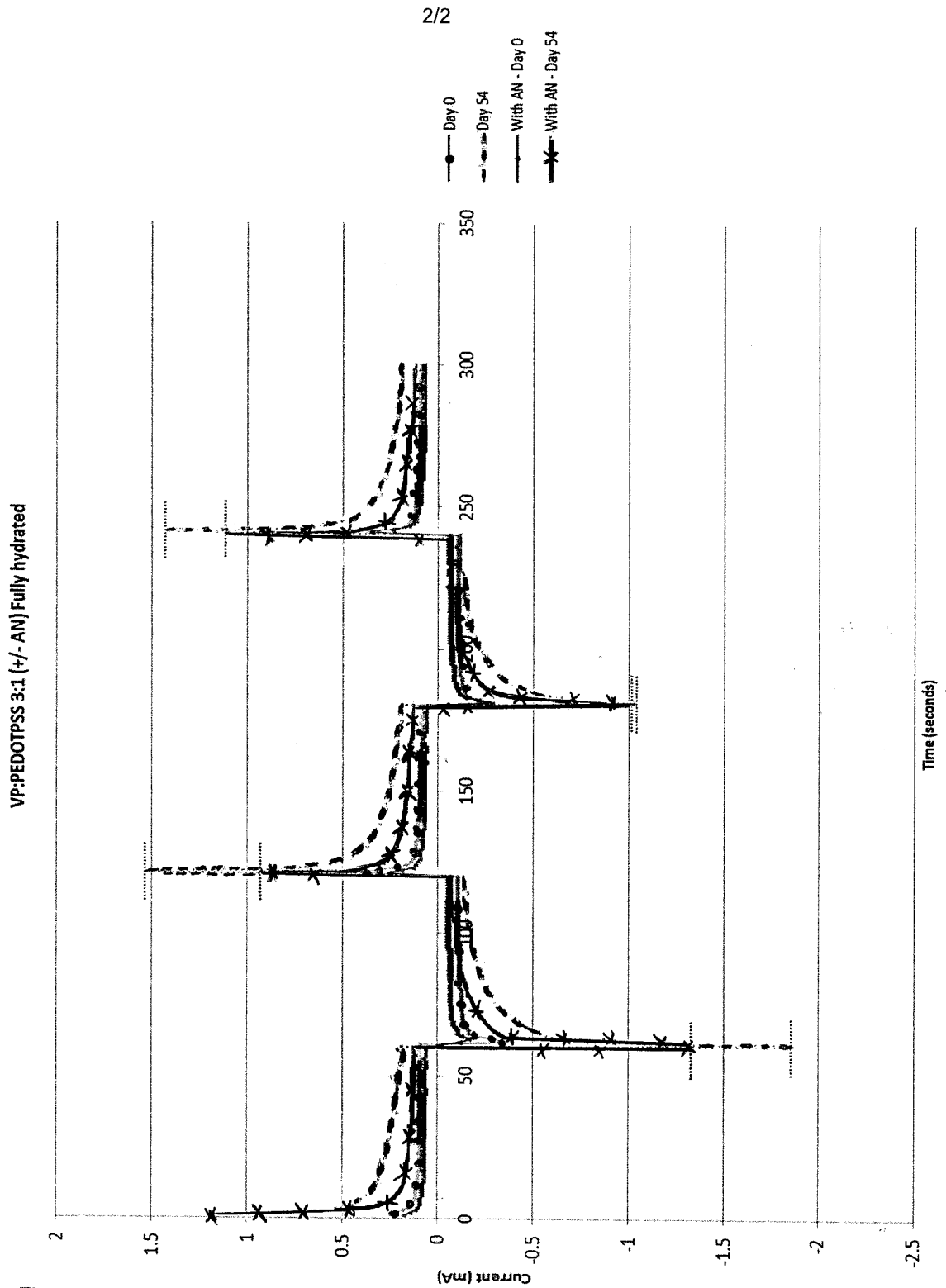


Figure 2 VP-PEDOTPSS 3:1 (with and without AN) after a maximum level of hydration was achieved