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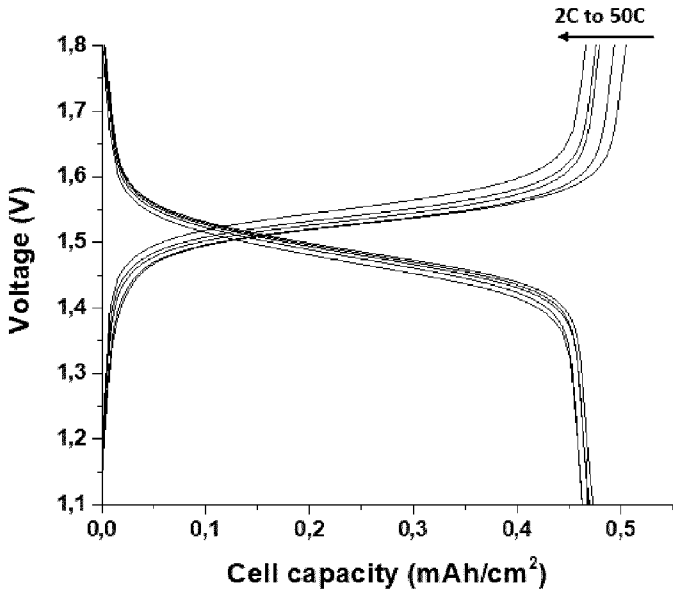

FIG.10

(57) Abstract: The present application relates biodegradable polymer material and electrochemical devices. More specifically, the present application relates to biodegradable polymer materials, their use in electrochemical devices and a method for preparing the same. More specifically, the biodegradable polymer material of the present application relates to comprises a polyester backbone; and redox active functionalities grafted to the polyester backbone, where the redox active functionalities may be selected from a stabilized radical species, a viologen species, a naphthalene diimide, and a quinone species.

[Continued on next page]

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BIODEGRADABLE BATTERIES WITH REDOX-ACTIVE POLYMER MATERIALS

CROSS REFERENCE TO RELATED APPLICATION

[0001] The present application claims the benefit of priority of co-pending U.S. Provisional Patent Application No. 63/522,622, which was filed June 22, 2023, the content of which is incorporated herein by reference in its entirety.

FIELD

[0002] The present application is in the field of biodegradable polymer material and batteries. More specifically, the present application relates to biodegradable polymer materials, their use in electrochemical devices such as batteries, and a method for preparing biodegradable batteries.

BACKGROUND

[0003] The number of batteries produced globally is on the rise. From portable and wearable electronics, internet of things (IoT) devices, patient healthcare monitoring, structural monitoring, environment monitoring, and smart packaging, new technologies require batteries to power embedded electronics. Consequently, there is an increasing demand for portable and remote power sources.

[0004] This increasing demand is problematic since there are currently no commercially available batteries that are environmentally friendly and/or biodegradable. Accordingly, there is a need to develop eco-friendly batteries.

[0005] Very few technologies have been developed with this issue in mind. Recently, a biodegradable battery technology has been proposed as a replacement for primary alkaline batteries, in which all components have been replaced by biodegradable analogues, except for the active materials themselves, typically metals or metal oxides (WO 2021/034899). Even though these batteries are substantially more environmentally friendly, they still contain metals and metals oxides that can pollute the environment.

[0006] Another avenue to increase the environmental sustainability of batteries is to replace commonly used inorganic elements such as metals and metal oxides with

organic-based active materials. For example, organic-based active materials that include redox active functionalities such as stable radicals and aromatic carbonyls are potential candidates for electrode active materials and alternatives to conventional metal oxides. (Nishide et al., *PureApplChem*, 2009; Schubert et al., *ChemSusChem*, 2019; Oyaizu et al., *J. Am. Chem. Soc.* 2018; Gaubicher et al., *Curr. Opin. Electrochem.*, 2018). The stable free radical 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) for instance exhibits fast and reversible charge/discharge reactions for 10^3 cycles rendering it ideal for incorporation into a cathode (Nishide et al., *Adv. Mater.* 2018; Oyaizu et al., *ACS Appl. Energy Mater.* 2019; Zhang et al. *Polymers*, 2019; Jia et al., *Polym. Chem.* 2016; Jia et al., *Polym. Chem.*, 2017). Electron-acceptor compounds, such as quinones and viologens can be used as anode active materials (Schubert et al., *ChemSusChem*, 2019). However, if these organic active materials are more desirable than metals and metal oxides for environment concerns, they are still not biodegradable and therefore do not fully resolve the issue of environmental pollution by battery waste.

[0007] Recently, biodegradable organic active materials have been proposed, based on polypeptides backbones and redox active functionalities (Nguyen et al., *Nature, 2021*). However, these materials being soluble in water, they can only be used with toxic organic electrolytes, which makes them unsuitable for a truly environmentally friendly and biodegradable battery.

[0008] As such, there is a need to provide biodegradable redox active materials that can be used in conjunction with environmentally benign aqueous electrolytes, and can be incorporated into entirely eco-friendly batteries.

SUMMARY

[0009] It has been shown herein that biodegradable polymer materials comprising a polyester backbone and redox active functionalities grafted to the polyester backbone are electrode active materials. The biodegradable polymer materials of the present application further provide electrode active materials that may be incorporated into a cathode and an anode of an aqueous battery.

[0010] Accordingly, the present application includes a biodegradable polymer material comprising: a polyester backbone; and redox active functionalities grafted to the polyester backbone.

[0011] Also included is the biodegradable polymer material of the present application for use as active material in an electrochemical device.

[0012] Further provided is an electrochemical device comprising a cathode, an anode, and an electrolyte, wherein: at least one of the cathode or the anode comprises a biodegradable polymer material of the present application as an active material, and the electrolyte is aqueous.

[0013] The present application also included an electrochemical device comprising a cathode, an anode, and an electrolyte wherein: the cathode comprises a first biodegradable polymer material as an active material, the anode comprises a second biodegradable polymer material as an active material and the electrolyte is aqueous.

[0014] Also provided is use of the biodegradable polymer material of the present application in an electrochemical device comprising a cathode comprising a first biodegradable polymer material as an active material; an anode comprising a second biodegradable polymer material as an active material; and an aqueous electrolyte.

[0015] Further provided is use of the biodegradable polymer material of the present application in an electrochemical device comprising a cathode comprising a biodegradable polymer material as an active material, wherein the radical species is TEMPO and the polyester backbone is polycaprolactone, an anode comprising a biodegradable polymer material as an active material, wherein the redox active functionalities are viologen species and the polyester backbone is polycaprolactone, and an aqueous electrolyte which comprises a metal salt or an organic salt.

[0016] The present application also includes a method for the preparation of a battery comprising the steps of: i) incorporating a first biodegradable polymer material as an active material into a cathode; ii) incorporating a second biodegradable polymer material as an active material into an anode; iii) assembling a battery cell comprising

the cathode, the anode and an aqueous electrolyte contained in a microporous separator or a solid polymeric gel. Other features and advantages of the present application will become apparent from the following detailed description. It should be understood, however, that the detailed description and the specific examples, while indicating embodiments of the application, are given by way of illustration only and the scope of the claims should not be limited by these embodiments, but should be given the broadest interpretation consistent with the description as a whole.

BRIEF DESCRIPTION OF DRAWINGS

[0017] The embodiments of the application will now be described in greater detail with reference to the attached drawings in which:

[0018] FIG.1 shows electrochemical characterization setup of a cell according to exemplary embodiments of the application.

[0019] FIG.2 shows an overlaid ATR-FTIR spectra of poly(α-chlorocaprolactone) (dark line) and poly(α-azidocaprolactone) (dashed line) according to exemplary embodiments of the application.

[0020] FIG.3 shows an overlaid ATR-FTIR spectra of poly(azido-caprolactone) (dashed line) and TEMPO-PCL (dark line) according to exemplary embodiments of the application.

[0021] FIG.4 shows a ^{1}H NMR spectrum of α-chlorocaprolactone according to exemplary embodiments of the application.

[0022] FIG.5 shows a ^{1}H NMR spectrum of poly(α-chlorocaprolactone) according to exemplary embodiments of the application.

[0023] FIG.6 shows a ^{1}H NMR spectrum of poly(α-azidocaprolactone) according to exemplary embodiments of the application.

[0024] FIG.7 shows a ^{1}H NMR spectrum of TEMPO-PCL according to exemplary embodiments of the application.

[0025] FIG.8 shows cyclic voltammogram at 20 mV/s illustrating electrochemical performances of TEMPO-PCL electrode in 1M zinc perchlorate according to exemplary embodiments of the application.

[0026] FIG.9A shows a charge and discharge galvanostatic cycle at 3 mA/cm^2 and FIG.9B shows the evolution of capacity and coulombic efficiency over the number of cycles, according to exemplary embodiments of the application.

[0027] FIG.10 shows galvanostatic cycles at different C-rates (2C to 50C). A 2C rate corresponds to 30 min of charge (or discharge) and 50C corresponds to 1/50 h of charge (or discharge) i.e. 1 min 12 s according to exemplary embodiments of the application.

[0028] FIG.11 shows cyclic voltammograms at 20 mV/s of a baseline carbon electrode (dashed lines) and a carbon electrode coated with pure TEMPO (full lines) according to exemplary embodiments of the application.

[0029] FIG.12 shows cyclic voltammogram at 20 mV/s of an electrode comprising a MV-grafted active material according to exemplary embodiments of the application.

DETAILED DESCRIPTION

I. Definitions

[0030] Unless otherwise indicated, the definitions and embodiments described in this and other sections are intended to be applicable to all embodiments and aspects of the present application herein described for which they are suitable as would be understood by a person skilled in the art.

[0031] The terms "about", “substantially” and “approximately” as used herein mean a reasonable amount of deviation of the modified term such that the end result is not significantly changed. These terms of degree should be construed as including a deviation of at least ±5% of the modified term if this deviation would not negate the meaning of the word it modifies or unless the context suggests otherwise to a person skilled in the art.

II. Materials of the Application

[0032] It has been shown herein that biodegradable polymer materials comprising a polyester backbone and redox active functionalities grafted to the polyester backbone are electrode active materials. The biodegradable polymer

materials of the present application further provide electrode active materials that may be incorporated into a cathode and an anode of a battery.

[0033] Accordingly, the present application includes a biodegradable polymer material that can be incorporated into battery electrodes, the material comprising a polyester backbone, and redox active functionalities grafted to the polyester backbone.

[0034] In some embodiments, the polyester backbone is poly(ε-caprolactone), poly(glycolic acid) (PGA), poly(lactic acid) (PLA), poly(para-dioxanone), poly(valerolactone), poly(ε-decalactone), poly(hydroxy valerate), poly(ethylene succinate), poly(ethylene adipate), poly(glycerol sebacate), poly(hydroxy butyrate) (PHB), or a polycarbonate (PC). In some embodiments the polyester backbone is a copolymer of the polyesters described above, such as poly(lactic-co-glycolic acid) (PLGA), poly(caprolactone-co-lactide) or poly(caprolactone-co-trimethylene carbonate).

[0035] In some embodiments, the polyester backbone is polycaprolactone or polycarbonate (PC). In some embodiments, the polyester backbone is polycaprolactone.

[0036] In some embodiments, the redox active functionalities are a stabilized radical species, a viologen species, a naphthalene diimide, or a quinone species.

[0037] In some embodiments, the radical species is 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO), a saturated or unsaturated proxyl, a spiro-dinitroxide, an arylnitroxide, an aryldinitroxide, a nitronylnitroxide, an iminoxyl, an acylnitroxide, a phenoxyl, a galvinoxyl, a verdazyl or a dithiadiazolyl. In some embodiments, the radical species is TEMPO, a saturated or unsaturated proxyl, or a spiro-dinitroxide. In some embodiments, the radical species is TEMPO or saturated or unsaturated proxyl. In some embodiments, the radical species is TEMPO.

[0038] In some embodiments, the viologen species is of formula $(C_5H_4NR)_2^{n+}$ wherein R represents a $(C_1\text{-}C_{12})$-alkyl group or in some embodiments R represents a $(C_1\text{-}C_6)$-alkyl group, or a $(C_1\text{-}C_3)$-alkyl group, and wherein n+ corresponds to the

degree of oxidation of the molecule. In some embodiments, the viologen species is $(C_5H_4NCH_3)_2^{n+}$ or $(C_5H_4NCH_2CH_3)_2^{n+}$. In some embodiments, n+ is 0, 1 or 2.

[0039] In some embodiments, the quinone species is 1,2-benzoquinone, 1,4-benzoquinone, 1,4-naphthoquinone, 9,10-anthraquinone, or derivatives thereof. In some embodiments, the quinone species is 1,2-benzoquinone or 1,4-benzoquinone.

[0040] In some embodiments, the redox active functionalities are grafted onto the polyester backbone through a linking moiety. It will be appreciated that the linking moiety is a chemical moiety suitable to form a covalent bond with the redox active functionality and form a covalent bond with the polyester backbone, thus attaching the redox active functionality and the polyester backbone to form the material. Various chemical moieties may be used as the liking moiety, depending on the synthetic chemical pathway used, and this would be within the purview of a skilled person in the art. In some embodiments, the linking moiety is a triazole, formed through the reaction of an azide group with a propargyl moiety (so-called “click chemistry”), as illustrated in Example 1.

[0041] In some embodiments, the biodegradable polymer material comprises the radical species TEMPO, the polyester backbone polycaprolactone and the linking moiety triazole.

[0042] In some embodiments, the biodegradable polymer material is a cathode active material. In some embodiments, the biodegradable polymer material is an anode active material.

III. Uses of the Application

[0043] The materials of the application have been shown to be electrode active materials for use in an electrochemical device, such as a battery or an electrochromic display.

[0044] Accordingly, the present application includes an electrochemical device comprising a cathode, an anode, and an electrolyte. In some embodiments, the electrochemical device is a battery.

[0045] In some embodiments, a biodegradable polymer material is incorporated into a cathode wherein the polymer material comprises redox active functionalities grafted to a polyester backbone and the redox active functionalities have an electrochemical potential suitable for a cathode material. In some embodiment, the redox active functionalities for a cathode material are TEMPO, saturated or unsaturated proxyls, spiro-dinitroxides, nitronylnitroxides, iminoxyls, acylnitroxides, phenoxyls, verdazyls or dithiadiazolyls.

[0046] In some embodiments, a biodegradable polymer material is incorporated into an anode, wherein the polymer material comprises redox active functionalities grafted to a polyester backbone and the redox active functionalities have an electrochemical potential suitable for an anode material. In some embodiment, the redox active functionalities for an anode material are viologens, arylnitroxides, galvinoxyl, naphthalene dimides, or quinones.

[0047] In some embodiments, the electrolyte is aqueous. In some embodiments, the aqueous electrolyte comprises a metal salt selected from the group of Li, Na, K, Mg, Ca, Zn, Mn, Ag and Fe. In some embodiments, the electrolyte salt is an ammonium salt, or a tetraalkylammonium salt. In some embodiments, the salt is a carbonate, a perchlorate, a sulfate, a sulfonate, a trifluorosulfonate, a fluorosulfonate, a tosylate, an imide, a trifluorosulfonylimide, a fluorosulfonylimide, a nitrate, an iodide, a chloride, a bromide, an acetate, a butyrate, a carboxylate, a formate, an oxalate, a lactate, a malonate, a tartrate, a tetrafluoroborate, a phosphate, an hexafluorophosphate, a phosphonate or a phosphinate. In some embodiments, the electrolyte contains of plurality of salts. In some embodiments, the electrolyte comprises an acid or a base. In some embodiments, the electrolyte comprises an acid or a base, and one or a plurality of salts. In some embodiments, the electrolyte salt is zinc perchlorate.

[0048] In some embodiments, the cathode is composed of i) a current collector layer; and ii) an active layer containing a biodegradable redox active polymer material suitable for a cathode, a conducting additive and a polymeric binder. In some embodiments, the current collector is flat. In some embodiments, the current collector

is a three-dimensional material and the active layer is incorporated in the three dimensions of the current collector.

[0049] In some embodiments, the anode is composed of i) a current collector layer; and ii) an active layer containing a biodegradable redox active polymer material suitable for an anode, a conducting additive and a polymeric binder. In some embodiments, the current collector is flat. In some embodiments, the current collector is a three-dimensional material and the active layer is incorporated in the three dimensions of the current collector.

[0050] In some embodiments, the anode is a metal or a metal alloy. In some embodiments, the anode comprises Zn, Mg or Ag. In some embodiments, the anode is composed of i) a current collector layer; and ii) an active layer containing metal or metal alloy particles, an optional conducting additive and a polymeric binder. In some embodiments, the current collector is flat. In some embodiments, the current collector is a three-dimensional material and the active layer is incorporated in the three dimensions of the current collector.

[0051] The present application further provides use of biodegradable polymer materials in an electrochemical device. The present application further provides use of biodegradable polymer materials in a battery. In some embodiments, the battery is a biodegradable battery. Accordingly, the present application includes uses of biodegradable polymer materials in a battery wherein the battery comprises a cathode comprising a first biodegradable polymer material, an anode comprising a second biodegradable material, and an aqueous electrolyte.

[0052] The present application further includes uses of biodegradable polymer materials in a biodegradable battery wherein the battery comprises i) a cathode comprising a biodegradable polymer material wherein the redox active species is TEMPO and the polyester backbone is polycaprolactone; ii) an anode comprising a biodegradable polymer material wherein the redox active functionalities are viologen, the polyester backbone is polycaprolactone; and iii) an aqueous electrolyte comprising a metal salt and/or an organic salt.

IV. Methods of the Application

[0053] The present application further includes a method for preparing a battery, the method comprising: i) incorporating a first biodegradable polymer material into a cathode as an active material; ii) incorporating a second biodegradable polymer material into an anode as an active material; iii) assembling a battery cell comprising the cathode, the anode and an aqueous electrolyte contained in a microporous separator or a solid polymeric gel.

[0054] In some embodiments, the biodegradable polymer material is incorporated into a cathode or an anode by formulating an ink comprising the biodegradable polymer material, a binder, conducting additives, and coating the ink onto a current collector. The binder is a polymer which is insoluble in the electrolyte of the battery and possesses good adhesion properties, as is typically known by people in the art. The binder can be polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), or styrene butadiene styrene rubber (SBR). In some embodiments, the binder is biodegradable, such as chitosan, cellulose acetate butyrate (CAB), an alginate or biodegradable polyesters as described in [0028]. In some embodiments, the binder is crosslinked to enable or enhance its insolubility in aqueous electrolytes and mechanical properties. Crosslinking methods include ion crosslinking by multivalent cations, or via the chemical reaction of crosslinking reactive functionalities such as acrylates or epoxy. Chemical crosslinking of reactive functionalities can be obtained by radiation curing (ultra-violet, electron beam, ...), thermal curing or chemical curing.

[0055] In some embodiments, the conducting additive is made of carbon materials, such as carbon black, graphite, graphene, single-wall carbon nanotubes (SWCNT), multi-wall carbon nanotubes (MWCNTs), vapour grown carbon fibers (VGCF) or carbon nanofibers (CNF). In some embodiments, the conducting additive is made of metals or alloys of Ag, Al, Cu, Ni, Ti or stainless steel, in the form of flakes, microfibers, nanofibers, microparticles or nanoparticles. In some embodiments, several conducting additives are incorporated into the ink.

[0056] The current collector is electronically conductive and can either be made of metal, a metal alloy or carbon. In some embodiments, the current collector is a flat

material such as a metal foil or a transparent sheet (made of plastic or glass) covered with a conductive layer such as indium tin oxide (ITO) or fluorine tin oxide (FTO). In some embodiments, the current collector is a three-dimensional material, such as a carbon paper, a carbon felt, a metal mesh or a metal foam. In some embodiments, the current collector is obtained by coating a conductive ink onto a non-conductive substrate, such as a paper or a plastic sheet. In some embodiments, the conductive ink is comprising conductive carbon materials, such as carbon black, graphite, carbon nanofibers, vapour grown carbon fibers (VGCF), carbon nanotubes (SWCNTs or MWCNTs) or graphene nanosheets. In some embodiments, the conductive ink is comprising metals or alloys of Ag, Al, Cu, Ni, Ti or stainless steel, in the form of flakes, microfibers, nanofibers, microparticles or nanoparticles. In some embodiments, several conducting additives are incorporated into the current collector ink.

[0057] In some embodiments, the microporous separator is made of a polymeric material insoluble in aqueous solutions, such as but not limited to: polyethylene, polypropylene, poly(vinylidene fluoride) (PVDF), polytetrafluoroethylene (PTFE), polyimide, polyamide, polyester, polyether sulfones, polysulfones, poly(vinyl chloride), polycarbonate, . In some embodiments, the microporous separator is biodegradable, such as cellulosic materials. In some embodiments, the microporous separator is made of glass fibers.

[0058] In embodiments, the electrolyte is a solid polymeric gel, replacing the microporous separator, such as described in US 2022/0149390. In some embodiment, the electrolyte is a biodegradable solid polymeric gel, such as described in WO 2021/034899.

[0059] In some embodiments, the battery is fabricated using printing methods, such as those described in WO 2021/034899.

EXAMPLES

[0060] The following non-limiting examples are illustrative of the present application.

General Methods

[0061] Unless stated otherwise, all reactions were performed under nitrogen atmosphere. All commercially available reagents were purchased from Sigma Aldrich and used as received without further purification. Reactions were monitored by TLC analysis using UV254 pre-coated TLC plates and visualized by staining with potassium permanganate solution.

[0062] Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were collected between 600 and 4000 cm^{-1} for 100 scans at a resolution of 4 cm-1 using a Bruker Tensor 27 FTIR spectrometer. Samples were run over a ZnSe crystal.

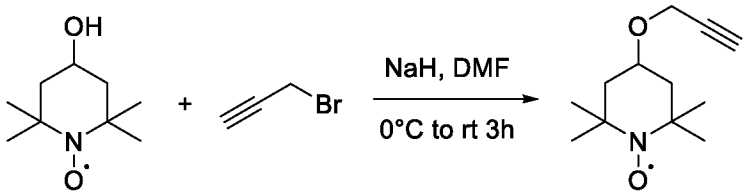
[0063] ^{1}H NMR spectra were obtained in the specified deuterated solvent using a Bruker AVANCE III 500 MHz spectrometer equipped with a 5 mm triple resonance probe with z gradient. The NMR data is presented as follow: chemical shift δ (ppm), multiplicity, coupling constant and integration. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, dd = doublet of doublet, ddd = doublet of doublet of doublet, m = multiplet.

[0064] Dynamic light scattering (DLS) and the zeta potential of the samples (2 mg/mL) in water were determined using a Zetasizer Nano-ZS (Malvern Instruments, Malvern, UK) in triplicate.

[0065] Electrochemical characterization was performed using a home-made electrochemical cell having either a 2-electrode or a 3-electrode configuration, with a microporous PTFE separator and filled with an aqueous electrolyte (FIG. 1). An Ag/AgCl reference electrode (3M NaCl) was used when using a 3-electrode configuration. Cells were tested on a Bio-Logic VMP3 multipotensiostat at ambient temperature.

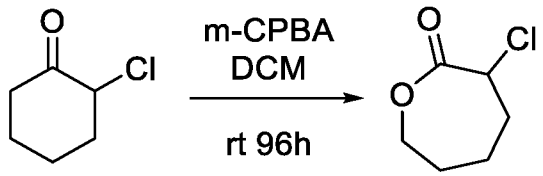
Example 1 – Synthesis of TEMPO-polycaprolactone (TEMPO-PCL)

[0066] *Synthesis of TEMPO-propargyl ether*



[0067] The procedure was adapted from Schulze and co-workers (*J. Mater. Chem. A*, 2020). Sodium hydride (866 mg, 21.25 mmol) was suspended in anhydrous dimethylformamide (DMF, 100 mL) in a flame dried 3-neck round bottom flask equipped with a magnetic stirrer. The resulting suspension was cooled down to 0 °C and 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (4-hydroxy-TEMPO, 3 g, 17.4 mmol) was added. The reaction mixture was stirred at 0 °C for 30 min and propargyl bromide solution (80% in toluene, 2.5 mL, 22.5 mmol) was added dropwise at 0 °C. After the addition, the reaction mixture was stirred at 0 °C for 1 h, then warmed to room temperature and stirred for another 3 h. The reaction mixture was quenched at 0 °C by adding water dropwise. Ethyl acetate (EtOAc) was added and layers were separated. The aqueous layer was extracted 3 times with EtOAc. Combined organic layers were washed 3× with water and once with brine, dried over Na_2SO_4, filtered and concentrated to a residue. The residue was purified by flash chromatography (0 – 10% EtOAc/hexanes) to afford 2.5 g (68% yield) of product as a bright orange solid. HRMS (ESI) calcd. for $C_{12}H_{20}NO_2Na$ [M+Na]: 233.1397, found 233.1383.

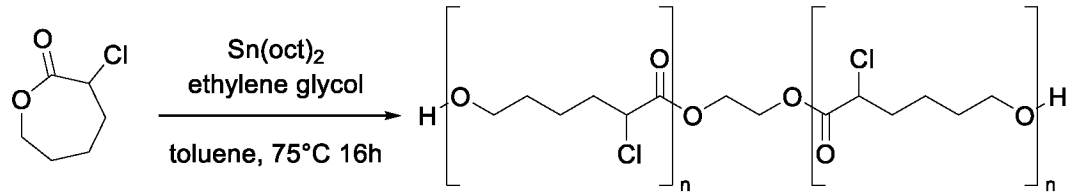
[0068] *Synthesis of α-chlorocaprolactone*



[0069] The procedure was adapted from Lenoir and coworkers (Macromolecules, 2004). In a 500 mL round bottom flask equipped with a magnetic stirrer was charged cyclohexanone (10 g, 75 mmol) in dichloromethane (DCM, 100 mL). 3-chloroperbenzoic acid (18 g, 81 mmol) was added and the resulting mixture was stirred at room temperature for 96 h while monitoring the progress by TLC. When all starting cyclohexanone was converted, solids were filtered from the reaction mixture and the cake was washed with cold DCM. The filtrate was cooled to -20 °C and stirred at this temperature for 2 h. Solids were filtered again and the filtrate was washed 3× with saturated sodium sulfite and saturated sodium bicarbonate solutions. The organic layer was dried over sodium sulfate, filtered and concentrated in vacuo to afford 7.2 g (64% yield) of a colorless oil that solidified upon freezing. The product was used for

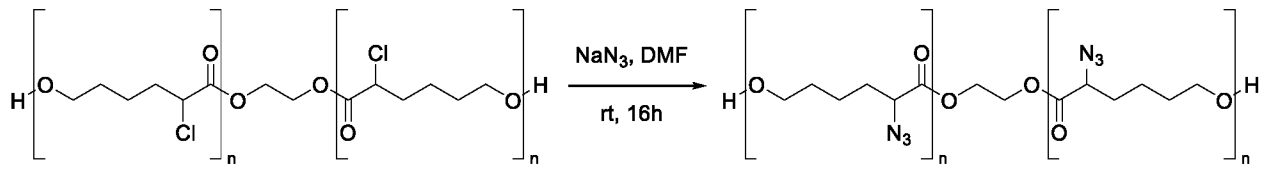
next step without further purification. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.81 (dd, *J1* = 2.5 Hz, *J2* = 8.2 Hz, 1H), 4.64 (ddd, *J1* = 1.8 Hz, *J2* = 7.9 Hz, *J3* = 12.7, 1H), 4.24 (ddd, *J1* = 1.5 Hz, *J2* = 7.5 Hz, *J3* = 12.7 Hz, 1H), 2.22-2.04 (m, 3H), 1.97-1.78 (m, 3H) ppm.

[0070] *Synthesis of poly(α-chlorocaprolactone)*



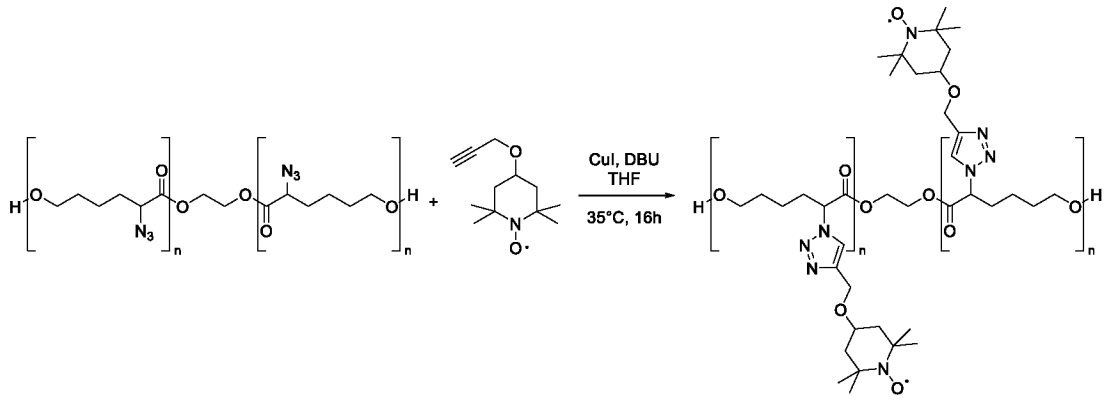
[0071] The procedure was adapted from Zhang and coworkers (*J. Polym. Sci. A Polym. Chem.* 2018). α-Chlorocaprolactone (1 g, 6.7 mmol) was dissolved in anhydrous toluene (5 mL) in a flame dried 25 mL round bottom flask. The resulting solution was purged with nitrogen gas for 10 min and $Sn(oct)_2$ (25 µL, 0.08 mmol) and ethylene glycol (5 µL, 9.42×10-4 mmol) were added to the reaction mixture. The flask was mounted with a water condenser and stirred at 120 °C overnight (oil bath was pre-heated before dipping the reaction mixture in). Solvents were removed under reduced pressure to afford 1 g of product as a clear colorless oil. The isolated oil was used as initiator in a subsequent polymerization reaction in order to increase the degree of polymerization. Poly(α-chlorocaprolactone) (200 mg) and α-chlorocaprolactone (1 g, 6.7 mmol) were dissolved in anhydrous toluene, and $Sn(oct)_2$ (43 µL, 0.014 mmol) was added. The reaction flask was mounted with a Dean-Stark trap and condenser and the mixture was stirred at 120 °C overnight. Solvent was removed in vacuo and the residue was dried on high vacuum overnight to afford a foam-like sticky solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.33-4.14 (m, 289.99H), 3.68 (m, 1H), 2.14-1.91 (m, 199.09H), 1.81-1.45 (m, 454.53H).

[0072] *Synthesis of poly(α-azidocaprolactone)*



[0073] The procedure was adapted from Riva and coworkers (*Macromolecules*, 2007). Poly(α-chlorocaprolactone) (860 mg) was dissolved in DMF (2.58 mL) in a 25 mL round bottom flask equipped with a magnetic stirrer. Sodium azide (70 mg) was added and the resulting mixture was stirred at room temperature overnight. The reaction mixture was extracted with DCM and washed with water. The organic layer was dried under reduced pressure to afford 744 mg of a semi-solid oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.29 (m, 1H), 4.21 (m, 1.67H), 3.87 (m, 0.16H), 3.67 (m, 0.39H), 2.03 (m, 1.96H), 1.63 (m, 4.72H) ppm. FTIR (cm^{-1}) 3470, 3028, 2955, 2870, 2110, 1740, 1458, 1366, 1275, 1215, 1167, 1111, 1034, 729, 696.

[0074] *Synthesis of TEMPO-polycaprolactone (TEMPO-PCL)*



[0075] The procedure was adapted from Riva and coworkers (*Macromolecules*, 2007). In a 25 mL round bottom flask, poly(α-azidocaprolactone) (744 mg), TEMPO-propargyl ether (1.21 g) and copper iodide (91 mg) were mixed together and purged with nitrogen. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 72 µL) was diluted in deoxygenated tetrahydrofuran (THF, 7.5 mL) and transferred to the reaction flask containing the reagents and catalyst. The reaction mixture was stirred at 35 °C overnight. Insoluble salts were removed by filtering the reaction mixture through a neutral alumina column. Solvents were removed under reduced pressure and the resulting crude oil was washed by suspending in methanol, followed by centrifugation and removal of the solvent. FTIR spectrum of the isolated product showed that the 2100 cm^{-1} peak seen in poly(azido-caprolactone), characteristic of azido groups, has disappeared. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.78 (s, 1H), 5.37 (s, 1H), 4.40-4.08 (m,

25H), 2.44-1.92 (m, 20H), 1.83-1.18 (m, 45H), 1.00-0.82 (m, 2H) ppm. FTIR (cm^{-1}) 3442, 3289, 2940, 1742, 1674, 1363, 1261, 1174, 1085, 1052.

Example 2 - Characterization of TEMPO-PCL

[0076] Utilizing PCL as a biodegradable substrate, redox-active (2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO) groups were grafted onto the polymeric chain through copper-catalyzed Huisgen's 1,3-dipolar cycloaddition or "click chemistry" reactions. Initially, TEMPO-propargyl ether was prepared by the reaction of hydroxyl-TEMPO with propargyl bromide, which introduces a terminal alkyne group on the TEMPO. In parallel, poly(α-azidocaprolactone) was prepared in two steps. First, α-chlorocaprolactone was polymerized to poly(α-chlorocaprolactone) with $Sn(oct)_2$, followed by replacement of the pendant chloro groups with azide groups as previously demonstrated by Riva and co-workers (*Macromolecules*, 2007). An isolated oil of poly(α-chlorocaprolactone) was used as initiator in a subsequent polymerization reaction in order to increase the degree of polymerization of the polymer to 192 (based on ^1H NMR calculation), which had the consistency of a sticky-solid. FIG. 2 shows the ATR-FTIR spectra of poly(α-chlorocaprolactone) and poly(α-azidocaprolactone) which shows the presence of a strong band at 2108 cm^{-1} for the N_3 functional group on the PCL backbone. Through click chemistry, the azido groups on poly(α-azidocaprolactone) were functionalized with the TEMPO group of TEMPO-propargyl ether (FIG. 3, ATR-FTIR spectra). Corroborating ^1H NMR spectra of α-chlorocaprolactone, poly(α-chlorocaprolactone), poly(α-azidocaprolactone), and TEMPO-PCL are presented in FIGS. 4-7, respectively to confirm synthesis of the intermediates and the final product.

Example 3 - Electrochemical properties of TEMPO-PCL

[0077] The electrochemical properties of the TEMPO-PCL were investigated by incorporating it into a carbon electrode (20 wt% TEMPO-PCL, 30% carbon black, 40 wt% graphite and 10 wt% PTFE binder). A 2-electrode cell was used, a zinc plate serving as a counter and reference electrode and a 1M zinc perchlorate aqueous solution as the electrolyte. The cyclic voltammogram (CV) a) shown in FIG. 9 demonstrated a very good cycling stability, and a high charge/discharge reversibility.

The material showed a capacity of 31 mAh/g (against a theoretical capacity of 70.3 mAh/g if all CL monomer units were to be grafted with TEMPO functionalities).

[0078] A Zn/TEMPO-PCL battery was assembled as a first demonstration of the technology. The battery comprised a Zn plate as an anode, a cathode comprising TEMPO-PCL as the active material (electrode formulation from Example 3 above), a microporous PTFE separator and a 1M aqueous zinc perchlorate electrolyte. The battery was tested using galvanostatic cycling. A typical charge-discharge profile b) is displayed on FIG. 9A, showing an operating voltage window between 1.4 V (discharged state) to 1.7 V (charged state). The cell could be cycled for more than 300 cycles with high coulombic reversibility and an overall 30% performance decay until zinc dendrites shorted the cell (FIG. 9B). Another cell was tested at various current densities (FIG. 10) and demonstrated a very high-power capability, delivering most of its energy in less than a minute.

[0079] Two types of control experiments are being showed in FIG. 11: a carbon electrode not incorporating the TEMPO-PCL redox active polymer and a carbon electrode having been coated with a TEMPO layer (from a TEMPO/acetone solution). The carbon electrode showed no electrochemical activity outside the double-layer charge stacking, giving a characteristic quasi-rectangular shape. On the other hand, the TEMPO-coated carbon electrode displayed the typical oxidation and reduction peaks of the TEMPO functionality, but rapidly decreasing in intensity along with the progressive detachment of the TEMPO moieties from the electrode. Those control experiments demonstrated that the TEMPO functionality is actually active and that it needs to be attached to the electrode to enable a stable cycling performance.

Example 4 – Prophetic biodegradable battery

[0080] A biodegradable battery is produced having i) a cathode comprising a redox active material having a suitable operating potential for a cathode, attached to a current collector using a biodegradable binder; ii) an anode comprising a redox active material having a suitable operating potential for an anode, attached to a current collector using a biodegradable binder; and iii) an aqueous electrolyte impregnated in

either a microporous film separating the anode and the cathode or a biodegradable solid gel electrolyte such as described in WO 2021/034899.

[0081] A biodegradable battery is produced having i) a cathode comprising a redox active material biodegradable polymer material with grafted TEMPO functionalities, having an operating potential of 1.3V – 1.7V vs. Zn/Zn^{2+} in a zinc perchlorate aqueous electrolyte, as shown on FIG. 8; ii) an anode comprising a biodegradable polymer material with grafted methyl viologen functionalities, having an operating potential of 0.2V – 0.6V vs. Zn/Zn^{2+} in a zinc perchlorate aqueous electrolyte, as shown on FIG. 12; and iii) a biodegradable aqueous solid gel electrolyte comprising a zinc perchlorate salt.

[0082] The biodegradable battery is expected to have an operating voltage between 1.5 V (charged state) and 0.7 V (discharged state), have the capability to be charged and discharged multiple times, and possess high power capability. The battery is expected to be substantially biodegradable and essentially free of heavy metals and metal oxides, making it particularly environmentally friendly.

[0083] While the applicant's teachings described herein are in conjunction with various embodiments for illustrative purposes, it is not intended that the applicant's teachings be limited to such embodiments as the embodiments described herein are intended to be examples. On the contrary, the applicant's teachings described and illustrated herein encompass various alternatives, modifications, and equivalents, without departing from the embodiments described herein, the general scope of which is defined in the appended claims.

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CLAIMS

1. A biodegradable polymer material comprising:

   a) a polyester backbone; and
   b) redox active functionalities grafted to the polyester backbone.

2. The biodegradable polymer material of claim 1, wherein the redox active functionalities are selected from a stabilized radical species, a viologen species, a naphthalene diimide, and a quinone species.

3. The biodegradable polymer material of claim 2, wherein the radical species is selected from the group consisting of 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO), a saturated or unsaturated proxyl, a spiro-dinitroxide, an arylnitroxide, an aryldinitroxide, a nitronylnitroxide, an iminoxyl, an acylnitroxide, a phenoxyl, a galvinoxyl, a verdazyl and a dithiadiazolyl.

4. The biodegradable polymer material of claim 2, wherein the viologen species is of formula $(C_5H_4NR)_2^{n+}$ wherein R represents a $(C_1\text{-}C_{12})$alkyl group.

5. The biodegradable polymer material of claim 2, wherein the quinone species is selected from the group consisting of 1,2-benzoquinone, 1,4-benzoquinone, 1,4-naphthoquinone, 9,10-anthraquinone and derivatives thereof.

6. The biodegradable polymer material of any one of claims 1 to 5, wherein the polyester backbone is selected from the group consisting of poly(ε-caprolactone), poly(glycolic acid) (PGA), poly(lactic acid) (PLA), poly(para-dioxanone), poly(valerolactone), poly(ε-decalactone), poly(hydroxy valerate), poly(ethylene succinate), poly(ethylene adipate), poly(glycerol sebacate), poly(hydroxy butyrate) (PHB), a polycarbonate (PC), poly(caprolactone-co-lactide), poly(caprolactone-co-trimethylene carbonate), and copolymers thereof.

7. The biodegradable polymer material of claim 3, wherein the radical species is TEMPO, saturated or unsaturated proxyl, spiro-dinitroxide or arylnitroxide.

8. The biodegradable polymer material of claim 2, wherein the radical species is TEMPO or saturated or unsaturated proxyl.

9. The biodegradable polymer material of claim 4, wherein the viologen species is $(C_5H_4NCH_3)_2^{n+}$ or $(C_5H_4NCH_2CH_3)_2^{n+}$, wherein n+ is 0, 1 or 2.

10. The biodegradable polymer material of claim 5, wherein the quinone species is 1,2-benzoquinone or 1,4-benzoquinone.

11. The biodegradable polymer material of claim 6, wherein the polyester backbone is polycaprolactone, or a polycarbonate (PC).

12. The biodegradable polymer material of claim 6, wherein the polyester backbone is polycaprolactone.

13. The biodegradable polymer material of any one of claims 1 to 12, wherein the redox active functionalities are grafted onto the polyester backbone through a linking moiety.

14. The biodegradable polymer material of any one of claims 1 to 13, wherein the radical species is TEMPO and the polyester backbone is polycaprolactone.

15. The biodegradable polymer material of any one of claims 1 to 14, for use as active material in an electrochemical device.

16. The biodegradable polymer material of any one of claims 1 to 15, wherein the biodegradable polymer material is an active material suitable to be applied as a cathode in an electrochemical device.

17. The biodegradable polymer material of any one of claims 1 to 15, wherein the biodegradable polymer material is an active material suitable to be applied as an anode in an electrochemical device.

18. An electrochemical device comprising a cathode, an anode, and an electrolyte, wherein:

at least one of the cathode or the anode comprises a biodegradable polymer material of any one of claims 1-14 as an active material, and

the electrolyte is aqueous.

19. An electrochemical device comprising a cathode, an anode, and an electrolyte wherein:

the cathode comprises a first biodegradable polymer material as an active material,

the anode comprises a second biodegradable polymer material as an active material and

the electrolyte is aqueous.

20. The electrochemical device of claim 19, wherein the cathode, the anode and the electrolyte are made of biodegradable materials to form a biodegradable electrochemical device.

21. The electrochemical device of any one of claims 18 to 20, wherein the device is a battery.

22. The electrochemical device of claim 19, wherein the first biodegradable polymer material comprises redox active functionalities and a polyester backbone.

23. The electrochemical device of claim 22, wherein the redox active functionalities are radical species.

24. The electrochemical device of claim 23, wherein the radical species are selected from the group consisting of 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO), a saturated or unsaturated proxyl, a spiro-dinitroxide, a nitronylnitroxide, an iminoxyl, an acylnitroxide, a phenoxyl, a verdazyl and a dithiadiazolyl.

25. The electrochemical device of claim 24, wherein the radical species is TEMPO, a saturated or unsaturated proxyl, a spiro-dinitroxide or an arylnitroxide.

26. The electrochemical device of claim 25, wherein the radical species is TEMPO or a saturated or unsaturated proxyl.

27. The electrochemical device of claim 22, wherein the polyester backbone is selected from the group consisting of poly(ε-caprolactone), poly(glycolic acid) (PGA), poly(lactic acid) (PLA), poly(paradioxanone), poly(valerolactone), poly(ε-decalactone), poly(hydroxy valerate), poly(ethylene succinate), poly(ethylene adipate), poly(glycerol sebacate), poly(hydroxy butyrate) (PHB), a polycarbonate (PC), poly(caprolactone-co-lactide), poly(caprolactone-co-trimethylene carbonate), and copolymers thereof.

28. The electrochemical device of claim 27, wherein the polyester backbone is polycaprolactone.

29. The electrochemical device of claim 19, wherein the second biodegradable polymer material comprises redox active functionalities and a polyester backbone.

30. The electrochemical device of claim 29, wherein the redox active functionalities are selected from a viologen species, arylnitroxides, a galvinoxyl, a naphthalene dimide, and a quinone species.

31. The electrochemical device of claim 30, wherein the viologen species is $(C_5H_4NCH_3)_2^{n+}$ or $(C_5H_4NCH_2CH_3)_2^{n+}$, wherein n+ is 0, 1 or 2.

32. The electrochemical device of claim 29, wherein the polyester backbone is selected from the group consisting of poly(ε-caprolactone), poly(glycolic acid) (PGA), poly(lactic acid) (PLA), poly(paradioxanone), poly(valerolactone), poly(ε-decalactone), poly(hydroxy valerate), poly(ethylene succinate), poly(ethylene adipate), poly(glycerol sebacate), poly(hydroxy butyrate) (PHB), polycarbonate (PC), poly(caprolactone-co-lactide), poly(caprolactone-co-trimethylene carbonate), and copolymers thereof.

33. The electrochemical device of claim 32, wherein the polyester backbone is polycaprolactone.

34. The electrochemical device of any one of claims 18-33, wherein the aqueous electrolyte comprises a metal salt, an organic salt or combinations thereof.

35. The electrochemical device of claim 34, wherein the metal of the metal salt is selected from the group consisting of Li, Na, K, Mg, Ca, Zn, Mn, Ag, Fe and combinations thereof.

36. The electrochemical device of claim 34, wherein the organic salt is selected from the group consisting of an ammonium salt, a tetraalkylammonium salt and combinations thereof.

37. The electrochemical device of any one of claims 34 to 36, wherein the salt is selected from a carbonate, a perchlorate, a sulfate, a sulfonate, a trifluorosulfonate, a fluorosulfonate, a tosylate, an imide, a trifluorosulfonylimide, a fluorosulfonylimide, a nitrate, an iodide, a chloride, a bromide, an acetate, a butyrate, a carboxylate, a formate, an oxalate, a lactate, a malonate, a tartrate, a tetrafluoroborate, a phosphate, an hexafluorophosphate, a phosphonate or a phosphinate and combinations thereof.

38. The electrochemical device of claim 33, wherein the aqueous electrolyte comprises zinc perchlorate.

39. Use of the biodegradable polymer material as defined in any one of claims 1 to 14 in an electrochemical device comprising

a cathode comprising a first biodegradable polymer material as an active material;
an anode comprising a second biodegradable polymer material as an active material; and
an aqueous electrolyte.

40. Use of the biodegradable polymer material as defined in any one of claims 1 to 14 in an electrochemical device comprising

a cathode comprising a biodegradable polymer material as an active material, wherein the radical species is TEMPO and the polyester backbone is polycaprolactone,

an anode comprising a biodegradable polymer material as an active material, wherein the redox active functionalities are viologen species and the polyester backbone is polycaprolactone, and

an aqueous electrolyte which comprises a metal salt or an organic salt.

41. A method for the preparation of a battery comprising the steps of:

i) incorporating a first biodegradable polymer material as an active material into a cathode;

ii) incorporating a second biodegradable polymer material as an active material into an anode;

iii) assembling a battery cell comprising the cathode, the anode and an aqueous electrolyte contained in a microporous separator or a solid polymeric gel.

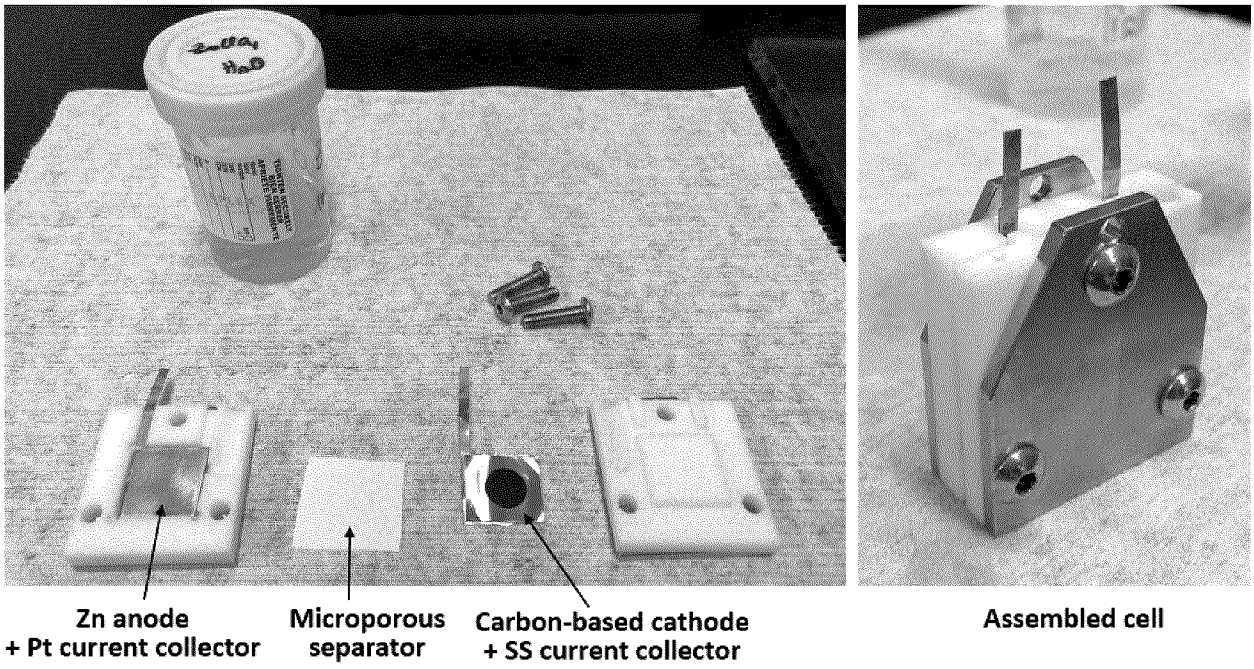
Zn anode
+ Pt current collector
Microporous
separator
Carbon-based cathode
+ SS current collector
Assembled cell

FIG. 1

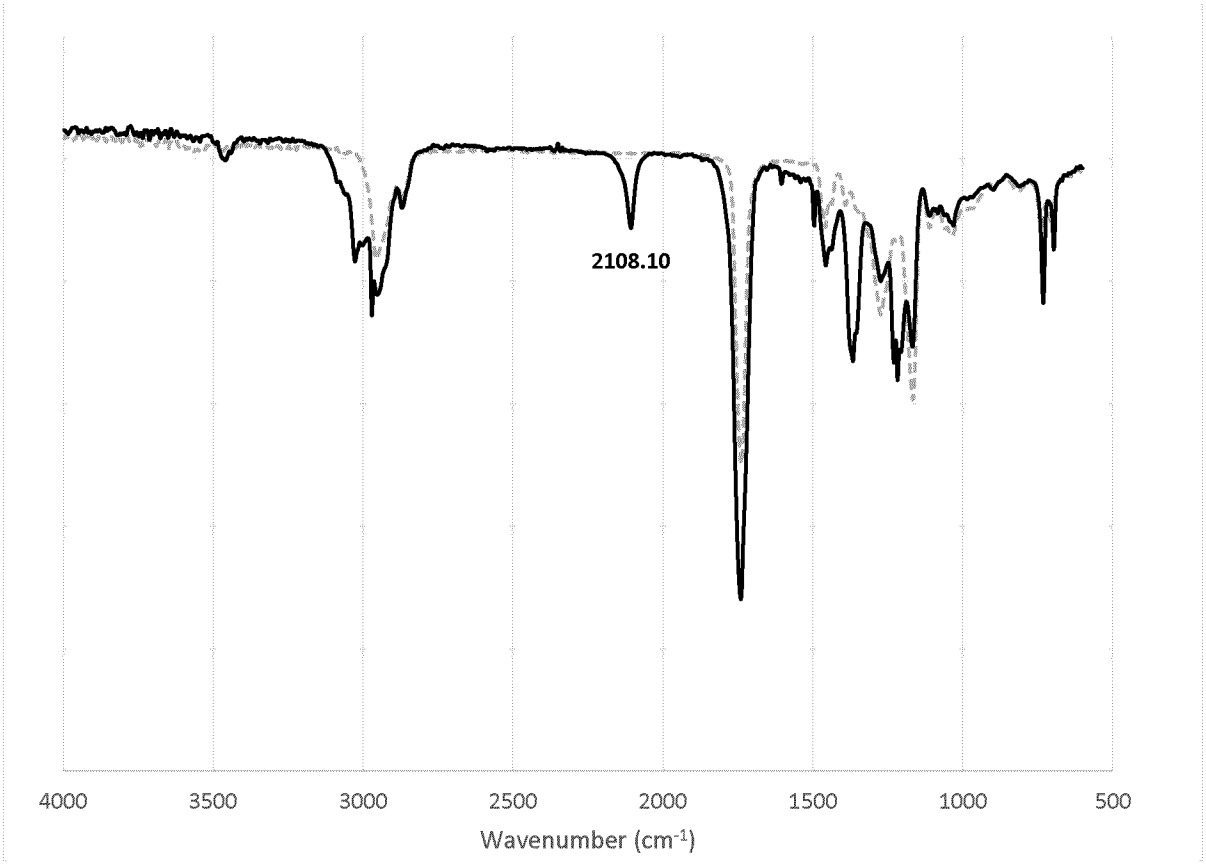
2108.10
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

FIG. 2

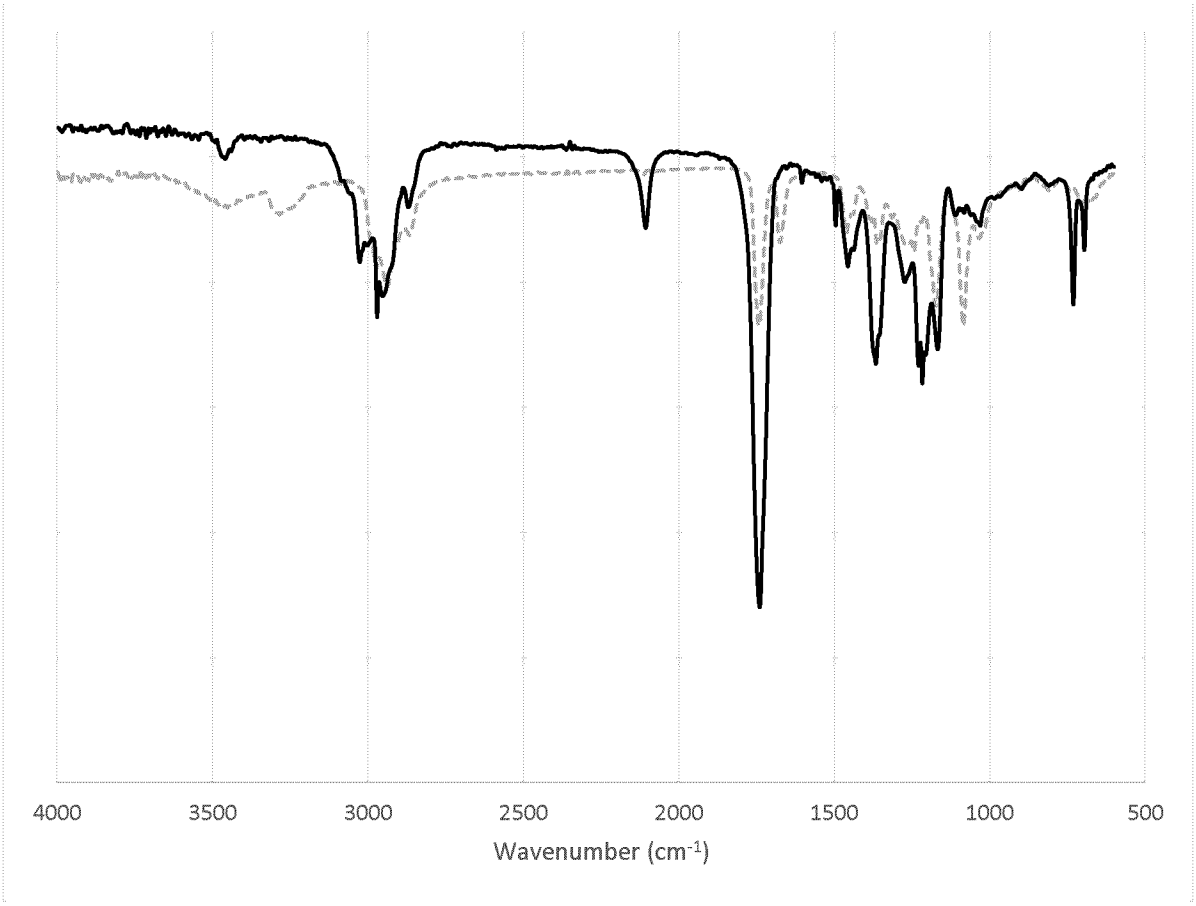

FIG. 3

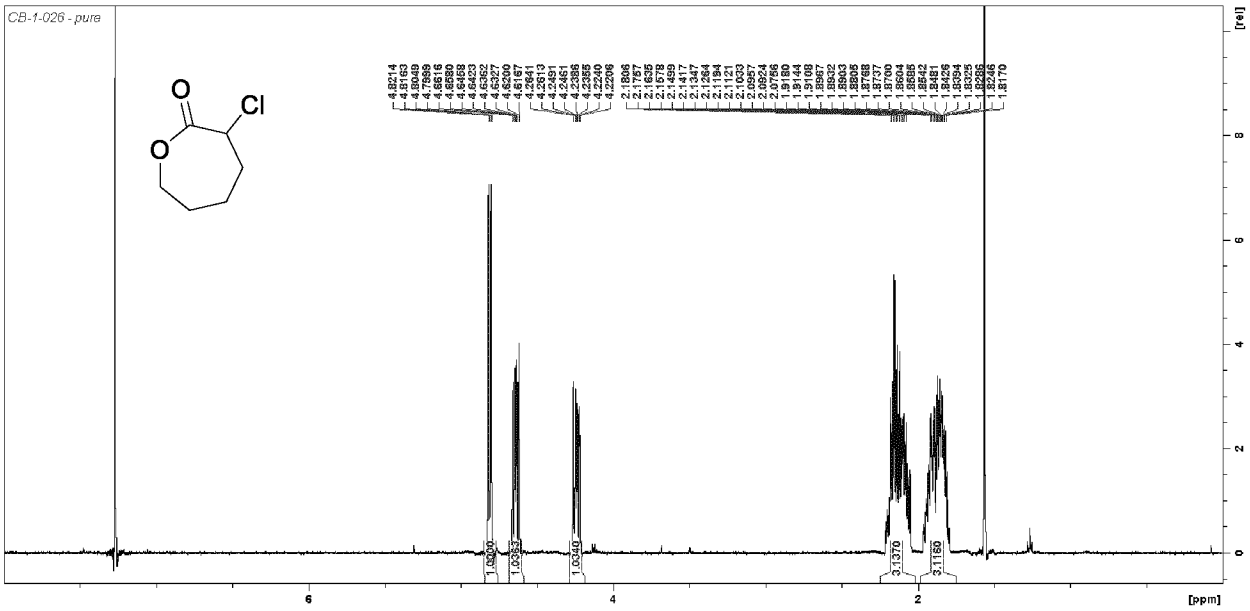

FIG. 4

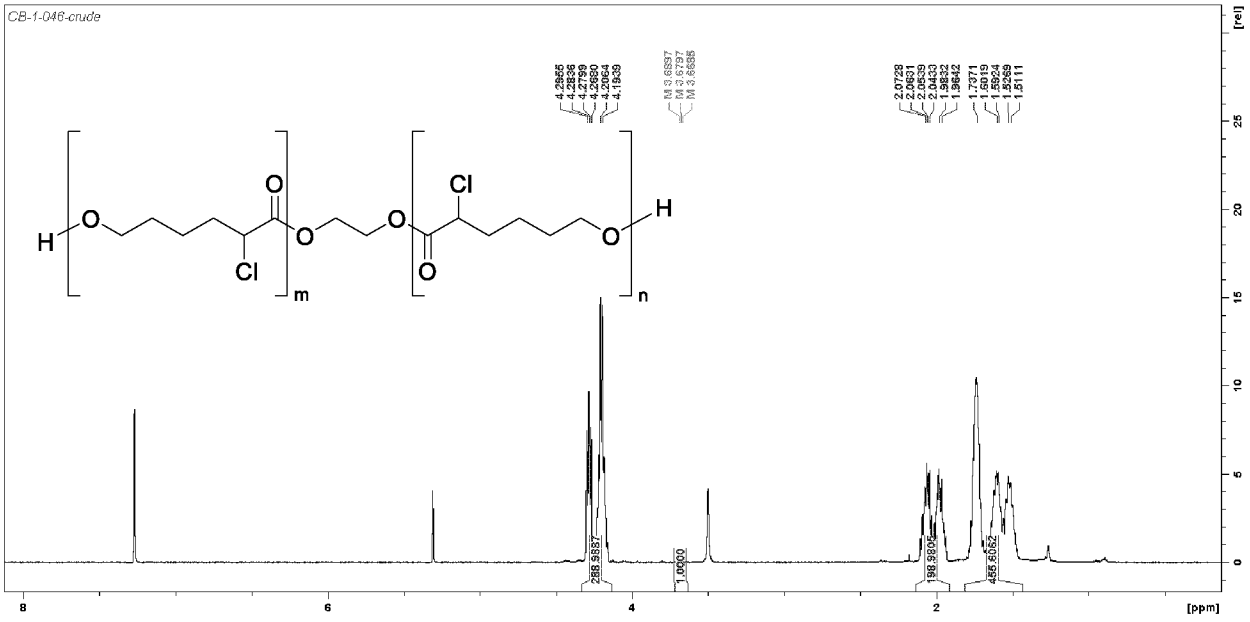

FIG. 5

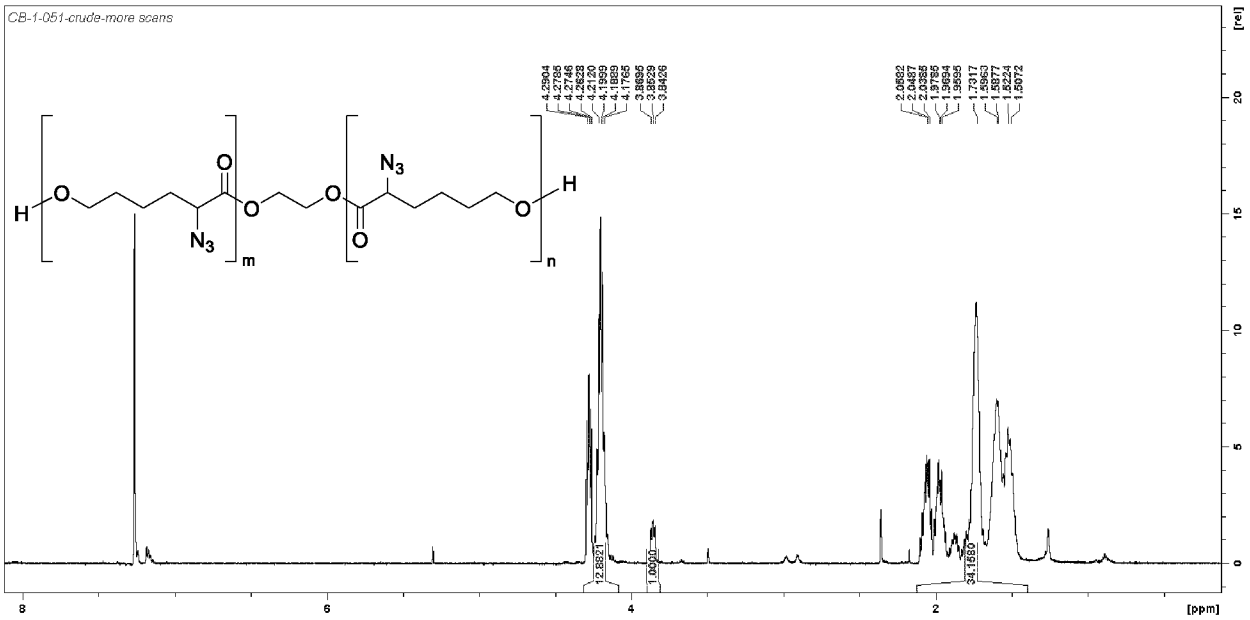
CB-1-051-crude-more scans
[rel]
[ppm]

FIG. 6

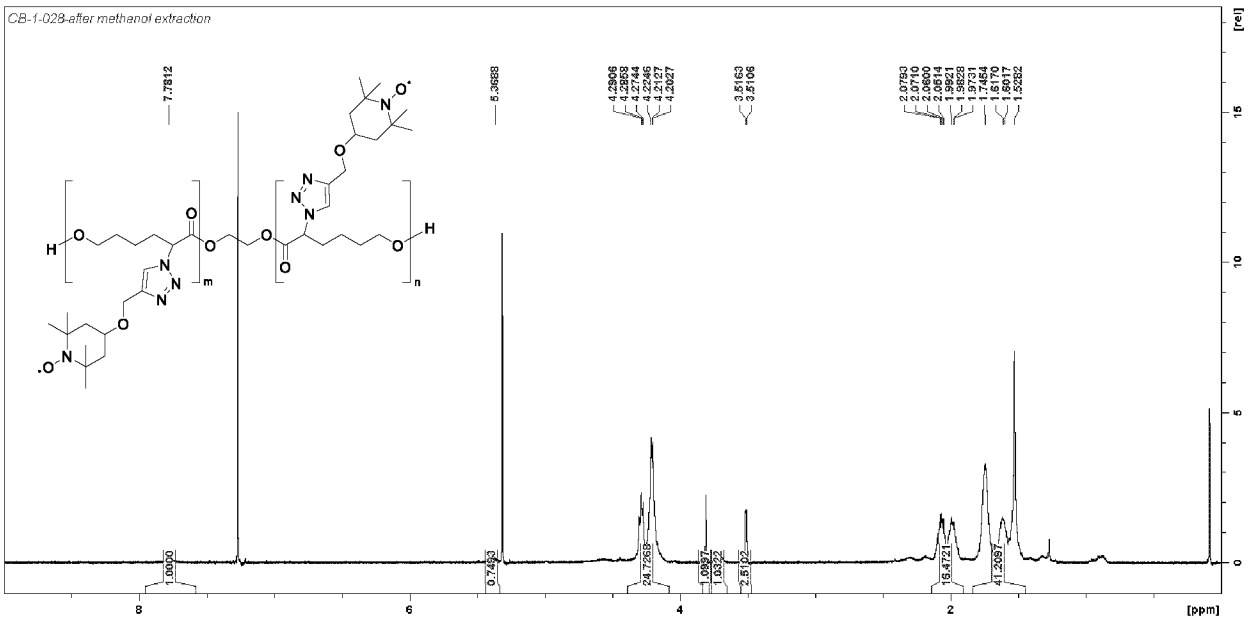
CB-1-028-after methanol extraction
[rel]
[ppm]

FIG. 7

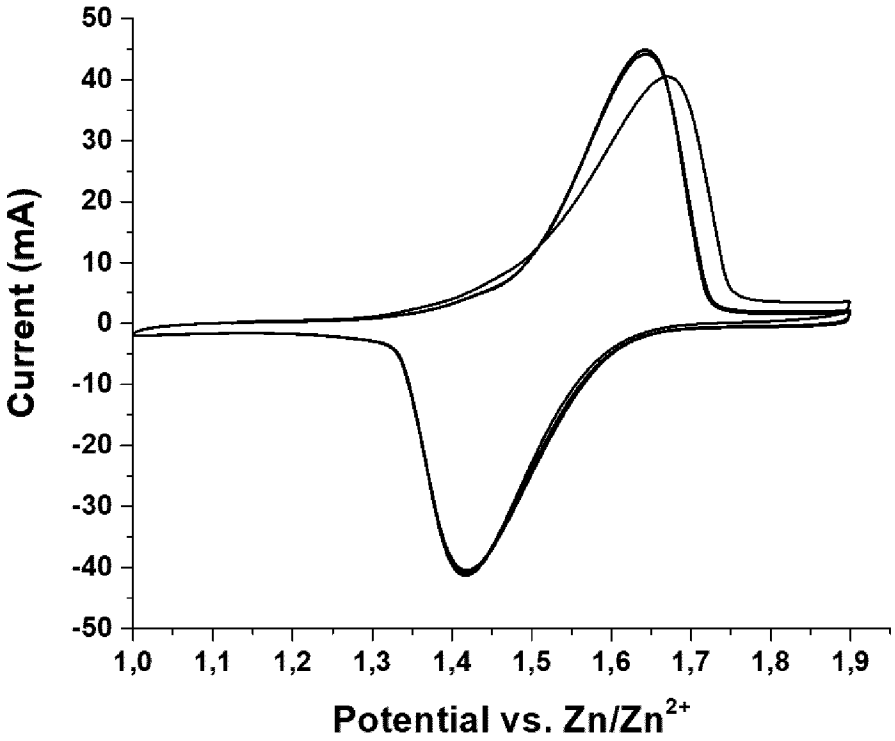
Current (mA)
50
40
30
20
10
0
-10
-20
-30
-40
-50
1,0
1,1
1,2
1,3
1,4
1,5
1,6
1,7
1,8
1,9
Potential vs. Zn/Zn2+

FIG. 8

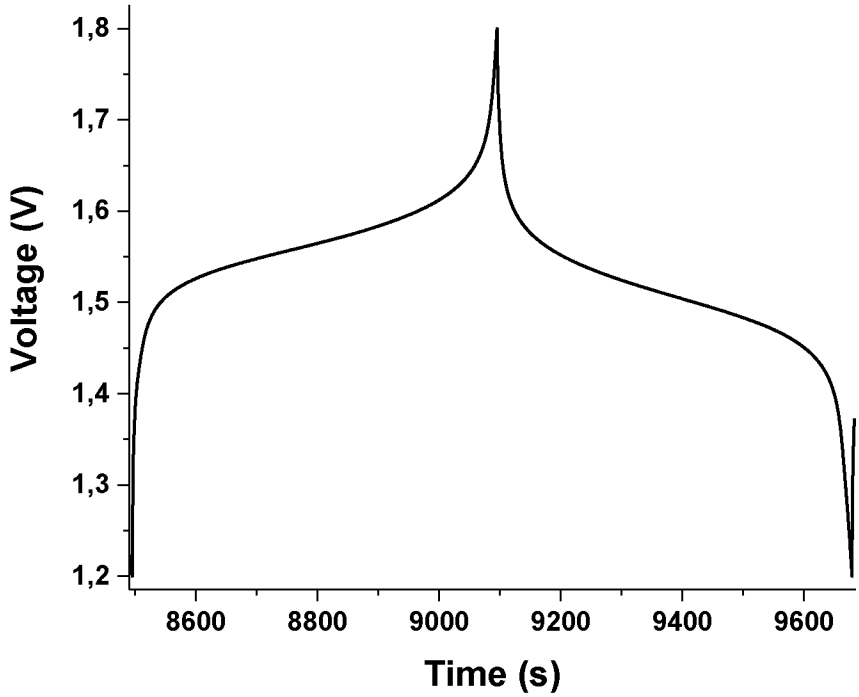
Voltage (V)
1,8
1,7
1,6
1,5
1,4
1,3
1,2
8600
8800
9000
9200
9400
9600
Time (s)

FIG.9A

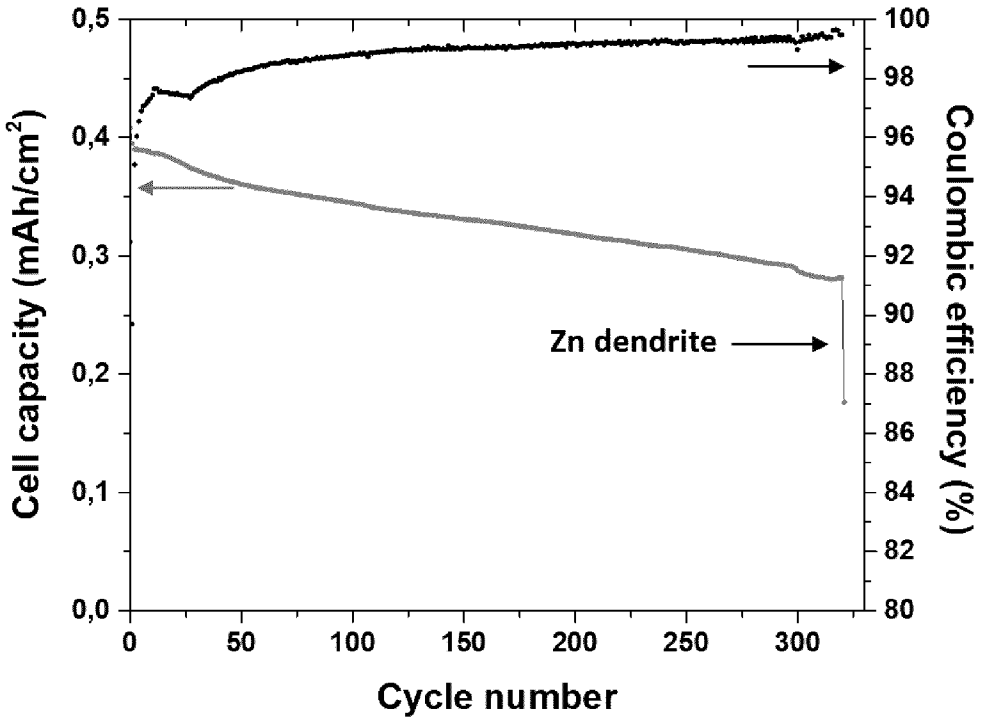
Cell capacity (mAh/cm^2)
0,5
0,4
0,3
0,2
0,1
0,0
Coulombic efficiency (%)
100
98
96
94
92
90
88
86
84
82
80
Zn dendrite
0
50
100
150
200
250
300
Cycle number

FIG.9B

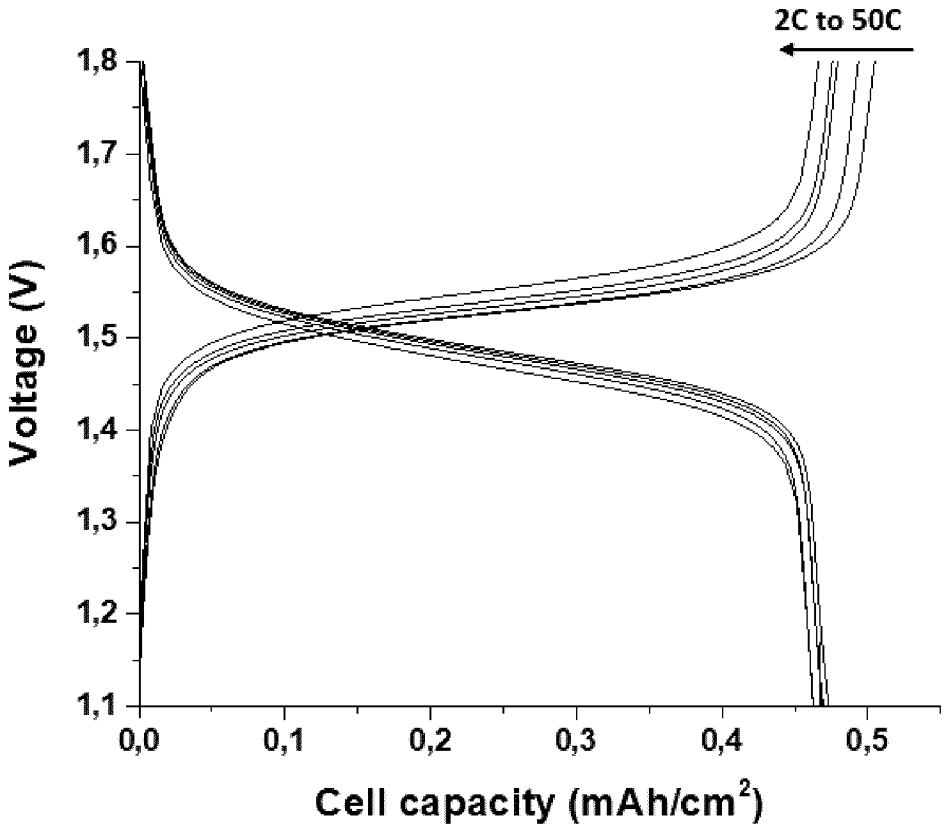
2C to 50C
1,8
1,7
1,6
1,5
1,4
1,3
1,2
1,1
Voltage (V)
0,0
0,1
0,2
0,3
0,4
0,5
Cell capacity (mAh/cm2)

FIG.10

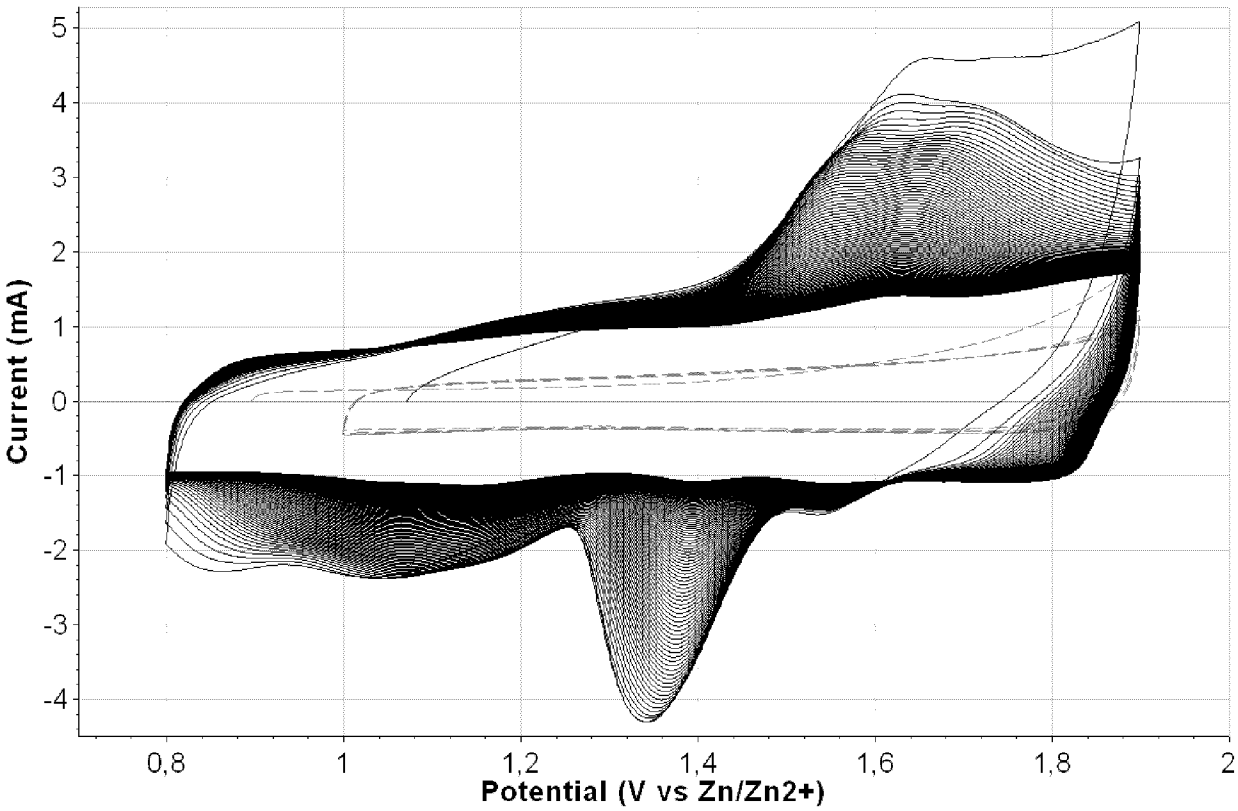

FIG. 11

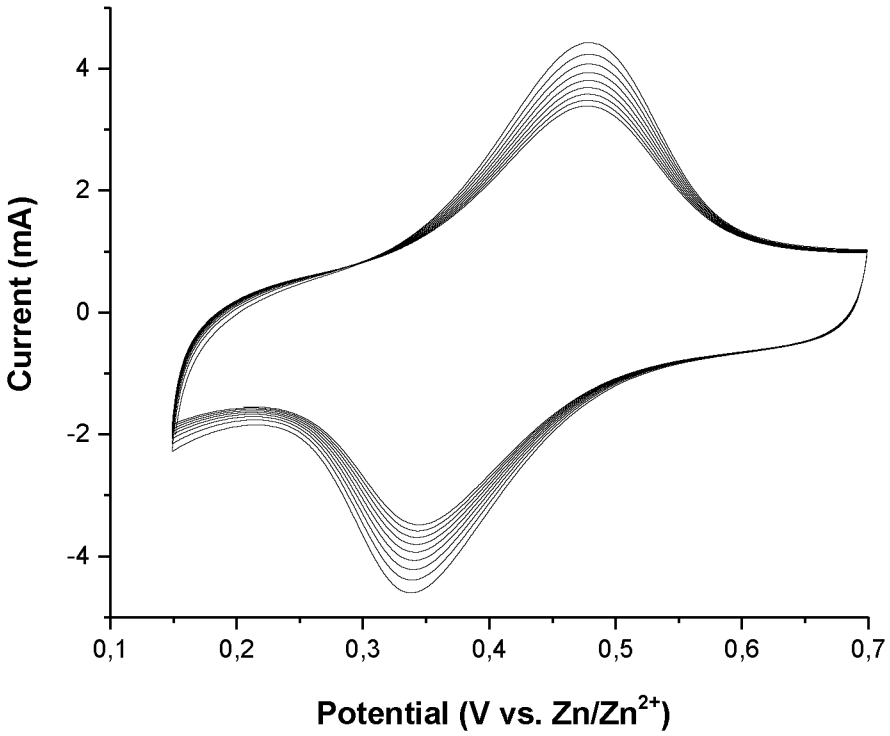

FIG. 12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2024/050576

A. CLASSIFICATION OF SUBJECT MATTER

IPC: ***C08G 63/91*** (2006.01) , ***H01M 4/06*** (2006.01) , ***H01M 4/60*** (2006.01) , *H01M 4/04* (2006.01)

CPC: **C08G 63/912** (2020.01) , H01M 4/06 (2020.01) , H01M 4/0492 (2020.01) , H01M 4/604 (2020.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC: ***C08G 63/91*** (2006.01), ***H01M 4/06*** (2006.01), ***H01M 4/60*** (2006.01), *H01M 4/04* (2006.01) CPC: **C08G 63/912** (2020.01)
CPC: **C08G 63/912** (2020.01), H01M 4/06 (2020.01), H01M 4/0492 (2020.01), H01M 4/604 (2020.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)

Databases: Questel Orbit (FAMPAT), Canadian Patent Database, Scopus
Search terms: "biodegradable", "anode", "cathode", "redox", "polyester", "graft", "benzoquinone", "caprolactone", "TEMPO", "viologen", "quinone"

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 3600411 A (CASSIDY, H.G. et al.) 17 August 1971 (17-08-1971) *col. 1, lines 45-71, col. 2, lines 20-29, 52-64, example 6*	1, 2, 5, 6, 10, 11, 13, 15 3, 4, 7-9, 12, 14, 16-41
X Y	PETROVA, S. et al., Synthesis and Solution Properties of PCL-*b*-PHPMA Diblock Copolymers Containing Stable Nitroxyl Radicals, Macromolecules 2016, Vol. 49, Pages 5407-5417 *abstract, scheme 1, page 5409-paragraph 2.2, figure 1*	1-3, 6-8, 11, 12, 14 4, 5, 9, 10, 13, 15-41
X Y	ZIIANG, J. et al., Synthesis of well-defined carboxyl poly(ϵ-caprolactone) by fine-tuning the protection group, Polymer Chemistry 2016, Vol. 7, Pages 4630 – 4637 *abstract, page 4633-left column, figure 7*	1-3, 6-8, 11-14 4, 5, 9, 10, 15-41

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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

Date of the actual completion of the international search 25 June 2024 (25-06-2024)	Date of mailing of the international search report 28 June 2024 (28-06-2024)
Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 819-953-2476	Authorized officer Raluca Aldea (819) 639-6935

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 2022/0052371 A1 (SCHUBERT, U. S.) 17 February 2022 (17-02-2022) *paragraphs [0058]-[0061]*	1, 15 2-14, 16-41
X	CN 112786894 A (PENG. H. et al.) 11 May 2021 (11-05-2021) *paragraphs [0004], [0005], claim 1, 2*	19-21, 41
Y	CN 114824398 A (WU, Y. et al.) 29 July 2022 (29-07-2022) *abstract, paragraphs [0003]-[0011], claims 1-3*	1-41

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CA2024/050576

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
US3600411A	17 August 1971 (17-08-1971)	US3707488A	26 December 1972 (26-12-1972)
US2022052371A1	17 February 2022 (17-02-2022)	CN113261135A	13 August 2021 (13-08-2021)
		DE102018009362A1	04 June 2020 (04-06-2020)
		EP3888174A2	06 October 2021 (06-10-2021)
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		WO2020108787A2	04 June 2020 (04-06-2020)
		WO2020108787A3	06 August 2020 (06-08-2020)
		ZA202103501B	26 October 2022 (26-10-2022)
CN112786894A	11 May 2021 (11-05-2021)	CN112786894B	11 October 2022 (11-10-2022)
CN114824398A	29 July 2022 (29-07-2022)	CN114824398B	25 July 2023 (25-07-2023)