(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
18 June 2015 (18.06.2015)

(10) International Publication Number
WO 2015/086078 A1

(51) International Patent Classification:
H01M 4/60 (2006.01) ***C07D 519/00*** (2006.01) ***H01M 10/0525*** (2010.01) *H01M 4/36* (2006.01) ***H01M 10/36*** (2010.01)

(21) International Application Number:
PCT/EP2013/076398

(22) International Filing Date:
12 December 2013 (12.12.2013)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicants: **TOYOTA MOTOR EUROPE NV/SA** [BE/BE]; Avenue du Bourget 60, B-1140 Brussels (BE). **UNIVERSITÀ DEGLI STUDI DI MILANO BICOCCA** [IT/IT]; Piazza dell'Ateneo Nuovo 1, I-20126 Milano (IT).

(72) Inventors: **ROSCIANO, Fabio**; Milcampslaan 127, B-1030 Schaarbeek (BE). **RUFFO, Riccardo**; Via Alessandro Volta 1, I-20099 Bresso (IT). **BEVERINA, Luca**; Via Gioacchino Murat 72, I-20159 Milano (IT). **SASSI, Mauro**; Via Sciesa 20, I-21040 Vedano Olona (IT). **SALAMONE, Matteo Marco**; Via Angelo Cazzaniga 161, I-20861 Brugherio (IT). **TOSI, Federico**; Via Giacomo Matteotti 44, I-21021 Angera (IT).

(74) Agents: **HART-DAVIS, Jason** et al.; Cabinet Beau De Lomenie, 158 Rue de l'Université, F-75340 Paris Cedex 07 (FR).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ,

[Continued on next page]

(54) Title: HIGH VOLTAGE ORGANIC MATERIALS FOR ENERGY STORAGE APPLICATIONS

(57) Abstract: The present invention relates to indolizine-based materials as energy storage materials in an electrochemical energy storage device. In preferred embodiments, said indolizine-based materials are obtained by electropolymerization, or chemical polymerization, of small molecule indolizines, in particular ones which have one or two indolizine ring systems.

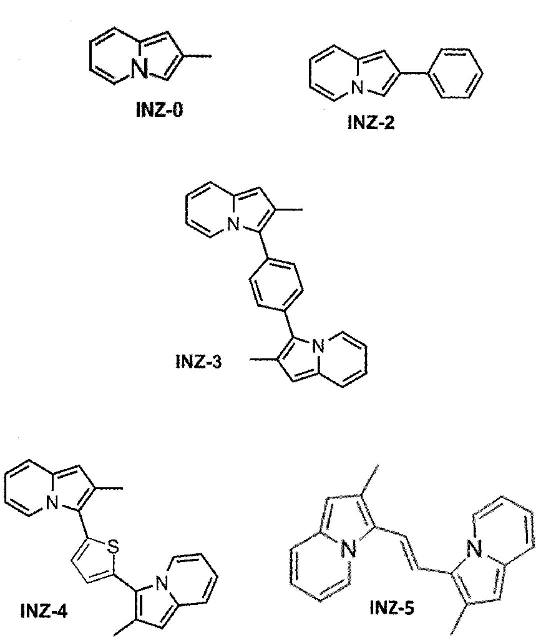


Figure 2

UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

High voltage organic materials for energy storage applications

Background to the Invention

Rechargeable (secondary) batteries are of increasing importance both in the consumer electronics field (as components of e.g. mobile telephones and laptop computers) as well as in vehicle and aerospace applications. An example of a rechargeable battery is the lithium-ion battery in which lithium ions in the electrolyte move from the negative electrode to the positive electrode during discharge (and move in the reverse direction during charging). Figure 1 shows an example of an electrochemical device used to store energy (a battery) containing a positive electrode material and a negative electrode material separated by separator containing a liquid, gel, polymeric or solid electrolyte, with a current collector used on both sides of the battery to carry the electrical energy.

Organic materials can be used effectively to store charge. Thus, US 2010/0009256 and US 2008/0038636 relate to the use of a polyradical material, a polymer with pendant nitroxyl radical groups, as an electrode active material. US 2003/0096165 discloses materials containing polyradicals of various structures for use in secondary batteries, and US 7045248 focuses on boron or sulfur radicals.

In order to increase the energy density of electrode materials for electrochemical energy storage, two strategies can be applied: (1) increase of the specific capacity Q (Ah/kg or Ah/L), or (2) increase of the electrochemical potential V at which the reaction occurs. The energy density (Wh/kg or Wh/L) is defined as $E = Q * V$, thus increasing V directly increases the energy density E.

Organic radicals based on the 2,2,6,6-tetramethylpiperidine-1-oxyl group (TEMPO) have been thoroughly investigated as cathode materials in organic batteries. This group shows an oxidation potential close to 3.6 V vs. Li^+/Li (Electrochimica Acta 2004 50(2-3) 827-831, also EP 1 128 453). Other materials have been used as possible cathode material for batteries, but their potential is lower than the above, such as dilithium rhodizonate (3 V vs Li^+/Li, ChemSusChem 2008 1 348-355); Tetracyanoquinodimethane (3 V vs. Li^+/Li, Scientific Reports 2012 2 453); or purpurin (3.2 V vs. Li^+/Li, Scientific Reports 2012 2 960).

Independently of the above, the use of indolizine in batteries has been described, but as cations of an ionic liquid to be used as electrolyte (EP 2169756, US 6472100).

Summary of the Invention

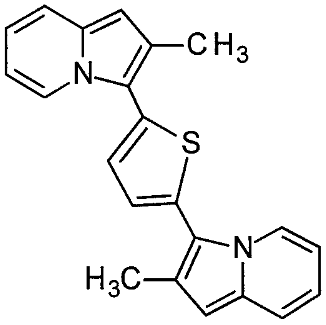
It is an object of the present invention to provide electrode materials for electrochemical energy storage, which have a high energy density, notably due to a high electrochemical potential. Molecules described herein comprising the indolizine structure offer an oxidation potential of 3.8 V vs. Li^+/Li, thus showing about a 10% improvement over the state of the art. The synthetic work of the present inventors has provided materials based on the indolizine structure that can be incorporated in an electrochemical energy storage device such as a battery.

In one aspect, the present invention therefore relates to a battery comprising a positive electrode, a negative electrode and an electrolyte therebetween, wherein either the positive electrode or the negative electrode contains an indolizine-based material. In preferred embodiments, the positive electrode / cathode contains the indolizine-based material.

In a further aspect, the invention relates to the use an indolizine-based material as an energy storage material in an electrochemical energy storage device.

In preferred embodiments, the said indolizine-based materials are obtained by electropolymerization, or chemical polymerization, of small molecule indolizines, in particular ones which have one or two indolizine ring systems. Advantageous indolizine ring substitution patterns for such molecules, that can be appropriately used in the framework of the present invention, will be set out in the detailed description of the invention that follows.

In a further aspect, the invention relates to the following compound:



which has been prepared in the context of the research of the present invention into new energy storage materials.

Brief Description of the Figures

Figure 1 shows an example of an electrochemical device used to store energy (a battery), in a schematic representation.

Figure 2 shows the structures of the five indolizine molecules specifically studied in the present invention.

Figure 3 is part of the prior art and shows electrochemical activity of the TEMPO organic radical.

Figure 4 shows electrochemical activity of all of the electropolymerized "poly"-indolizines specifically studied in the present invention.

Figure 5(a-e) shows the electropolymerization of all the indolizine molecules specifically studied in the present invention.

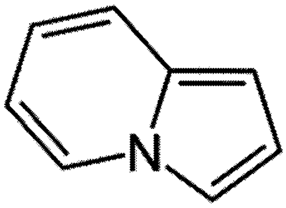
Figure 6(a-e) shows the electrochemical characterization of all the indolizine-based layers obtained by electropolymerization process.

Figure 7 shows an example of battery performances obtained using the INZ-5-based layer obtained by electropolymerization as positive electrode material.

Figure 8 shows an example of a typical charge-discharge curve of a "metal-free" battery obtained using the INZ-4 active material as cathode and the NPbIm-1 active material as anode, and a 1M tetrabutylammonium perchlorate solution in acetonitrile as electrolyte.

Detailed Description of the Invention

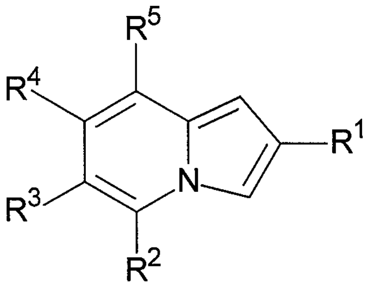
The indolizine molecule, without any substitution, has the following structure:



The indolizine core ring system, because of its high potential operation and low molecular weight, may enable a theoretical capacity of 230 mAh/g to be obtained. However, the molecule should appropriately be modified and functionalized in order to be useful for energy storage.

Modifications of the indolizine molecule may *inter alia* help to increase the operation potential and/or to improve the stability towards electrochemical oxidation and reduction.

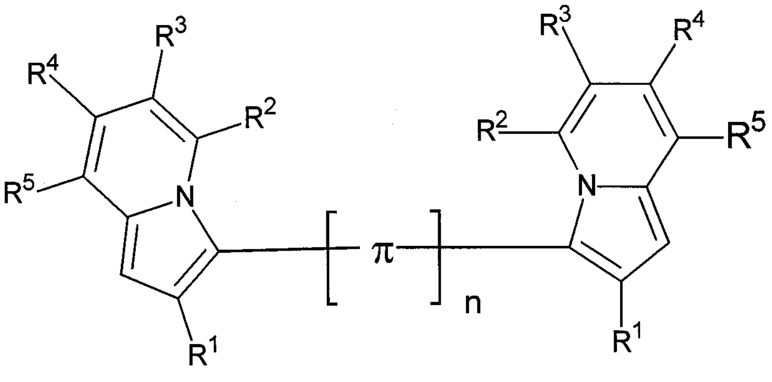
The generic structure of the molecules used in this invention can be summarized as shown in the following two schematic diagrams. The first diagram (formula (I)) shows a single indolizine-ring containing molecule that can be used as the basis of polymers having said indolizine as repeating units, according to the present invention:



(I)

Advantageously, in the present invention, in above formula (I), the 5-membered ring positions are not substituted (bearing only hydrogen (H) atoms), apart from the carbon atome bearing the R^1 group, because these positions on the 5-membered ring are involved in polymerization, important in the preparation of indolizine-based materials for energy storage purposed in the present invention.

The following, second diagram (formula (II)) shows a class of molecules having two indolizine rings connected through a conjugated bridge. Such molecules can also be polymerized to give polymers having said indolizines as repeating units:



(II)

In both structures, R^1 can be a hydrogen atom or any linear or branched alkyl chain, or glycolic chain, having from 1 to 8 carbon atoms, an ester whose alcoholic residue is an alkyl chain which is linear or branched having up to 8 carbons / an ester having up to 10 carbon atoms in all, a benzene ring, or a naphthalene ring substituted at the 1 or 2 position. For example, in advantageous embodiments R^1 may be -Me or $-C_6H_5$, -Me being particularly preferred. R^2, R^3, R^4, and R^5 may be substituents including, without being limited to, the following: H, methyl, branched or linear alkyl chains up to 8 carbon atoms, halogens, esters and amides preferably with 8 or less carbon atoms, alkyl and aryl nitriles preferably with 8 or less carbon atoms, nitro derivatives, sulfones and sulfoxides, perfluoroalkyl preferably with 8 or less carbon atoms, alkoxy groups, dialkylamino, diarylamino, phenyl, 1-naphthyl, 2-naphthyl. The reference π of formula (II) indicates a conjugated bridge, which may be a double bond, a triple bond, or a plurality of double or triple bonds conjugated in a number of 2 or 3, e.g. a benzenic ring, a thiophenic ring, a furane ring and a pyridine ring. Such rings can be functionalized with residues having the same nature as substituents R^2-R^4. In advantageous embodiments, π may comprise a (carbon-carbon) double bond e.g. π may be -CH=CH-, which may be in a trans configuration), or a phenyl ring, for example $-C_6H_4$-, for example in a para- (or meta-) substitution pattern. Alternatively, π may be a conjugated heterocyclic system such as a 2,5-thienyl bridge. n in formula (II) is an integer of at least 1, and is preferably equal to 1.

In the experimental work of the present invention, five specific examples of modified indolizines were prepared and the electrochemical behavior of polymers derived therefrom was studied. Synthesis of the materials is contained in part A of the experimental examples section below, while the polymerization protocols are contained in part B. The structures of the five indolizine molecules specifically studied in the present invention are shown in Figure 2.

In order to prepare indolizines for use as electrochemical energy storage materials, these may be converted into polymers. This can be done according to the standard scheme of oxidative polymerization of electron-rich heterocycles, through the use of oxidizing agents the likes of: Iron(III) salts, cerium ammonium nitrate, iodine, ammonium persulfate and in general any oxidizing agent able to generate the radical cation of the aforementioned indolizine monomers.

In a typical secondary battery, a negative electrode layer and a positive electrode layer are separated via a separator containing an electrolyte. A positive electrode collector may be attached to the positive electrode layer, and a negative electrode collector may be attached to the negative electrode layer.

The negative electrode collector and the positive electrode collector may be a metal foil or metal plate made of, for example, nickel, aluminum, copper, gold, silver, an aluminum alloy and stainless steel; a mesh electrode; and a carbon electrode. The collector may be active as a catalyst or an active material may be chemical bound to a collector. A separator made of a porous film or a nonwoven fabric may be used for preventing the above positive electrode from being in contact with the negative electrode. The separator may, for example, be made of polyethylene or polypropylene, or glass fiber.

The indolizine-based organic active material of the invention is preferably used at the positive electrode. It is possible to combine the indolizine-based organic active material with other, known positive electrode active materials. Such species may include lithium manganates such as $LiMnO_2$ and $Li_xMn_2O_4$ $(0<x<2)$, lithium manganates having a Spinel structure, MnO_2, $LiCoO_2$, $LiNiO_2$, $Li_yV_2O_5$ $(0<y<2)$, olivine materials $LiFePO_4$, and materials in which a part of Mns in Spinel structure are substituted with another transition metal.

As materials for the negative electrode layer, these may appropriately include carbon materials such as graphite and amorphous carbon, lithium metal or a lithium alloy, lithium-ion occluding carbon and conductive polymers. Film, bulk, granulated powder, fiber and flake forms of such materials may be used. Apart from lithium, other metals may be used at the negative electrode, such as sodium and magnesium. It is also possible to use calcium, silver, copper and aluminum as metal anodes.

In advantageous embodiments of the present invention, the positive electrode or the negative electrode (most preferably the positive electrode) contains at least 50 % by mass of the indolizine-based material, more preferably at least 60 % by mass, still more preferably at least 70 % by mass, even more preferably at least 80 % by mass, and even in some embodiments at least 90 % by mass.

A conductive auxiliary material or ion-conductive auxiliary material may be added for reducing an impedance during forming an electrode layer comprising the indolizine-based organic active material of the invention (normally in the positive electrode), and/or in the opposite electrode. Examples of such a material include carbonaceous particles such as graphite, carbon black and acetylene black and conductive polymers such as polyaniline, polypyrrole, polythiophene, polyacetylene and polyacene.

A binder may be used for reinforcing binding between components in either electrode. Examples of sutable binders include polyvinylidene fluoride, a copolymer of vinylidene fluoride and hexafluoropropylene, a copolymer of vinylidene fluoride and tetrafluoroethylene, polytetrafluoroethylene, a copolymer rubber of styrene and butadiene, and resin binders such as polypropylene, polyethylene and polyimide.

An electrolyte contained in the battery transfers charged carriers between the electrodes, and may be prepared by, for example, dissolving an electrolyte salt in a solvent. Examples of such a solvent include organic solvents such as ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, methyl ethyl carbonate, γ-butyrolactone, tetrahydrofuran, dioxolane, sulforane, dimethylformamide, dimethylacetamide, N-methyl-2-pyrrolidone, acetonitrile. Other possibilities inlcude sulfones (e.g. ethyl-methyl sulfone), sulfoxides (DMSO, dimethylsulfoxide), ethers such as tetraglyme. In this invention, these solvents may be used alone or in combination of two or more. Examples of an electrolyte salt include $LiPF_6$, $LiClO_4$, $LiBF_4$, $LiCF_3SO_3$, $LiN(CF_3SO_2)_2$, $LiN(C_2F_5SO_2)_2$, $LiC(CF_3SO_2)_3$ and $LiC(C_2F_5SO_2)_3$. Non-metal electrolyte salts include tetrabutylammonium (TBA) salts such as TBA-ClO_4.

An electrolyte may be solid. Examples of a polymer used in the solid electrolyte include vinylidene fluoride polymers such as polyvinylidene fluoride, a copolymer of vinylidene fluoride and hexafluoropropylene, a copolymer of vinylidene fluoride and ethylene, a copolymer of vinylidene fluoride and monofluoroethylene, a copolymer of vinylidene fluoride and trifluoroethylene, a copolymer of vinylidene fluoride and tetrafluoroethylene and a terpolymer of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene; acrylonitrile polymers such a copolymer of acrylonitrile and methyl methacrylate, a copolymer of acrylonitrile and methyl acrylate, a copolymer of acrylonitrile and ethyl methacrylate, a copolymer of acrylonitrile and ethyl acrylate, a copolymer of acrylonitrile and methacrylic acid, a copolymer of acrylonitrile and acrylic acid and a copolymer of acrylonitrile and vinyl acetate; polyethylene oxide; a copolymer of ethylene oxide and propylene oxide; and polymers of these acrylates or methacrylates. The polymer may contain an electrolyte solution to form a gel or the polymer may be used alone.

A secondary battery in the present invention may have a conventional configuration, where, for example, an electrode laminate or rolled laminate is sealed in, for example, a metal case, a resin case or a laminate film made of a metal foil such as aluminum foil and a synthetic resin film. It may take a shape of, but not limited to, cylindrical, prismatic, coin or sheet.

A secondary battery according to the present invention may be prepared by a conventional process. For example, a slurry of an active material in a solvent is applied on an electrode laminate and the product is piled with a counter electrode via a separator. Alternatively, the laminate is rolled and placed in a case, which is then filled with an electrolyte solution.

In the present invention, there is disclosed an electrochemical energy storage device (e.g. a battery) where at least one of the electrodes is based on the indolizine (INZ) structure. In particular, the indolizine-based material may appropriately be used at the positive electrode. Depending on the choice of electrolyte, the negative electrode can appropriately be a metal (e.g. Li, Na, Mg), an intercalation material (e.g. graphitic carbon or a ceramic such as $Li_4Ti_5O_{12}$), a lithium conjugated aromatic carboxylate material (e.g. as described by Walker at al., J. Mater. Chem., 2011, 21, 1615-1620), or another organic material (e.g. Naphthalene Bisimide, NPbIm). The electrolyte can be a liquid, a polymer, a solid or a combination of these. In particular, when using two organic materials as electrodes, the salt dissolved in the electrolytic solution can be organic (i.e. no need for metallic cations such as Li^+, Na^+, Mg^{2+}), thus allowing one to build a completely metal-free battery.

An embodiment of the invention features the indolizine-based material at the cathode, naphthalene bisimide at the anode and an electrolytic solution such as 1M tetrabutylammonium perchlorate ($TBAClO_4$) dissolved in acetonitrile (ACN). The battery cathode can be prepared by mixing a powder of an INZ material, a conductive additive such as graphitic carbon, and a polymeric binder such as styrene-butadiene rubber in water, thus obtaining a slurry. The slurry can then be cast on an aluminum foil, and dried. After drying, the electrode can be cut and shaped as desired. An analogous process can be employed to prepare the anode, by using a powder of NPbIm in place of INZ. The dried electrodes may appropriately be placed facing each other, a separator such as glass fiber or polyethylene interposed between them, the whole assembly then being flooded with the electrolytic solution. The battery assembly may appropriately be enclosed in an air-tight environment such as a pouch or a can and sealed.

Upon charging the battery, the cathode material is oxidized and the charge is compensated by the anions of the electrolytic solution; at the same time the anode is reduced and the charge is compensated by the cations of the electrolytic solution. The operation of the battery can be summarized as following:

$$\begin{array}{ccccc} \mathrm{INZ} & \xrightarrow{\text{Charge}} & \mathrm{INZ^{+}\,{}^{-}ClO_4} & \xrightarrow{\text{Discharge}} & \mathrm{INZ} \\ \mathrm{NPbIm} & & \mathrm{NPbIm^{-}\,{}^{+}TBA} & & \mathrm{NPbIm} \end{array}$$

Upon discharge, the compensating ions are released back in the solution, and INZ and NPbIm go back to their original state, thus providing reversible, rechargeable battery performance.

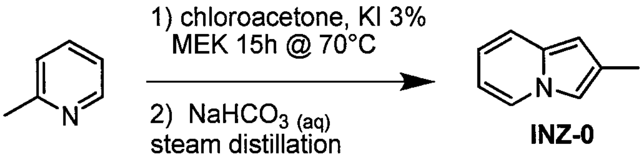
Within the practice of the present invention, it may be envisaged to combine any features or embodiments which have hereinabove been separately set out and indicated to be advantageous, preferable, appropriate or otherwise generally applicable in the practice of the invention. The present description should be considered to include all such combinations of features or embodiments described herein unless such combinations are said herein to be mutually exclusive or are clearly understood in context to be mutually exclusive.

Experimental section – Examples

The following experimental section illustrates experimentally the practice of the present invention, but the scope of the invention is not to be considered to be limited to the specific examples that follow.

Part A: Synthesis of INZ materials

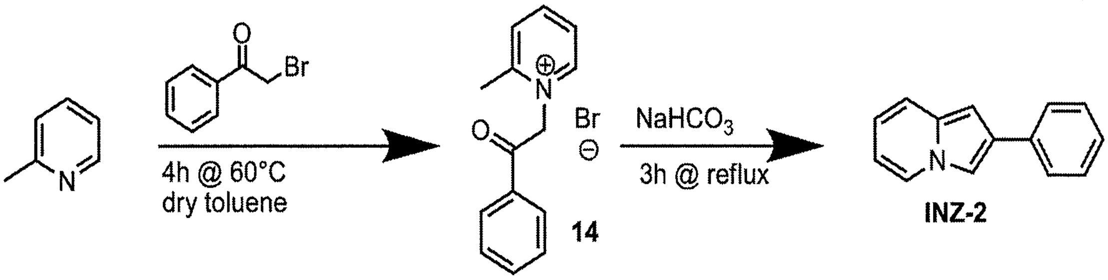
1. Synthesis of INZ-0



In an amber glass 50 ml RBF, equipped with $CaCl_2$ guard tube, chloroacetone (10.34 ml, 11.91 g, 128.7 mmol) was added to a solution of 2-picoline (10.00 g, 107.3 mmol) in 2-butanone (25 ml) followed by KI (641 mg, 3.86 mmol). The mixture was heated to 70°C for 15 h, cooled to RT and kept under stirring for 12 h. Et_2O (25 ml) was added to the mixture and the obtained suspension was filtered on an Hirsh funnel. The deliquescent dark solid was transferred to a 250 ml RBF and dissolved in 125 ml of water. The solution was kept under stirring and $NaHCO_3$ was slowly added observing gas evolution. The mixture was steam distilled obtaining a suspension of the pure product in the distillate. The distillate was filtered on an Hirsh funnel and the white solid was dried under reduced pressure at room temperature (8.305 g, 63.3 mmol, yield 59%).

^1H NMR δ (ppm, 500.13 MHz, $CDCl_3$): 7.83 (dd, 1H, j = 7.0, j = 0.8); 7.31 (d, 1H, j =9.0); 7.14 (s, 1H); 6.66-6.62 (m, 1H); 6.43-6.40 (m, 1H); 6.30 (s, 1H); 2.40 (s, 3H).

2. Synthesis of INZ-2



2.1 Synthesis of 14

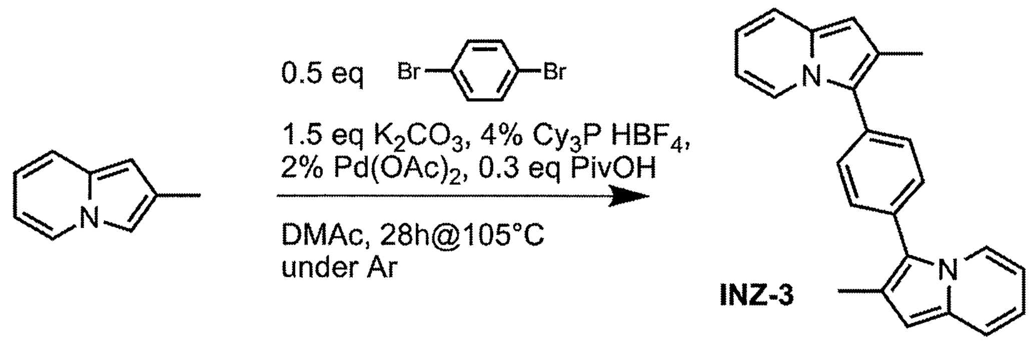
In a 250 ml RBF, equipped with reflux condenser and $CaCl_2$ guard tube, bromoacetophenone (3.52 g, 37.8 mmol) was added portion wise to a solution of 2-picoline (7.52 g, 37.8 mmol) in dry toluene (90 ml). The obtained solution was stirred at 60°C for 4 h. Pure product was obtained as a white precipitate that was collected by filtration (10.22 g, 34.98 mmol, yield 92.5%).

2.2 Synthesis of INZ-2

Product **14** (10.22 g, 34.98 mmol) was refluxed for 3h in a solution of $NaHCO_3$ (3.04 g, 36.19 mmol) in water (150 ml). Product was obtained as a grey precipitate, collected by filtration, and dried under reduced pressure (m.p. 211°C).

^{1}H NMR δ (ppm, 500.13 MHz, $CDCl_3$): 7.89 (d, 1H, j = 6.9); 7.67 (d, 2H, j = 7.6); 7.58 (s, 1H); 7.40 (t, 2H, j = 7.6); 7.35 (d, 1H, j = 9.0); 7.26 (t, 1H, j = 7.4) 6.70 (s, 1H); 6.66 (t, 1H, j = 6.8); 6.46 (t, 1H, j = 6.7)

3. Synthesis of INZ-3

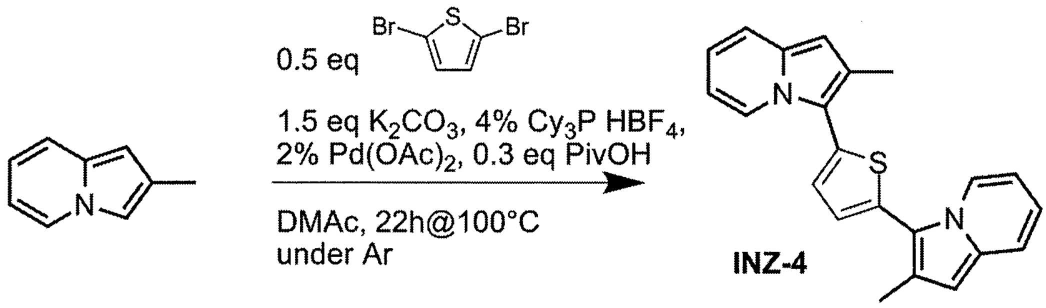


INZ-3

In a screw-capped glass pressure cylinder (total volume 120 ml) a mixture of K_2CO_3 (3.160 g, 22.870 mmol), 1,4-dibromobenzene (1.798 g, 7.624 mmol), Cy_3P HBF_4 (224 mg, 0.610 mmol), $Pd(OAc)_2$ (68.4 mg, 0.305 mmol) and pivalic acid (467 mg, 4.57 mmol) is prepared in air. The tube is transferred to an Ar-filled glove-box and 2-methylindolizine (2.000 g, 15.24 mmol) is added to the mixture followed by 50 ml of anhydrous DMAc. The tube is tightly closed with a Teflon cap and heated to 105°C in a heating bath for 28h. The mixture is allowed to cool to RT, poured in water (200 ml) and extracted with AcOEt (150 ml). The organic phase is collected, washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. The crude product is purified by column chromatography (eluent: toluene/n-hexane 1:1). Product is obtained as light grey powder (735 mg, 2.185 mmol, yield 28%).

^1H NMR (500 MHz, CD_2Cl_2) δ [ppm]: 8.19 (d, J=7.1 Hz, 2H), 7,64 (s, 4H), 7,38 (d, J=9.0 Hz, 2H), 6.71 (m, 2H), 6.58-6.33 (m, 4H), 2.43 (s, 6H)
^{13}C NMR (125.7 MHz, CD_2Cl_2) δ [ppm]: 133.42, 131.35, 130.84, 124.34, 123.07, 123.009, 119.25, 117.84, 110.61, 101.85, 13.14.

4. Synthesis of INZ-4



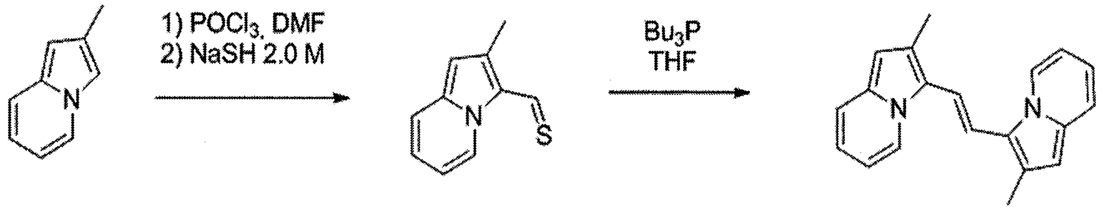
In a screw capped glass pressure cylinder (total volume 120 ml) a mixture of K_2CO_3 (1.580 g, 11.43 mmol), Cy_3P HBF4 (112 mg, 0.305 mmol), $Pd(OAc)_2$ (34.2 mg, 0.52 mmol) and pivalic acid (234 mg, 2.29 mmol) is prepared in air. The tube is transferred to an Ar-filled glove-box, 2-methylindolizine (1.000 g, 7.62 mmol) and 2,5-dibromothiophene (922.2 g, 3.81 mmol) are added to the mixture followed by 15 ml of anhydrous DMAc. The tube is tightly closed with a Teflon cap and heated to 100°C in an heating bath for 22h. The mixture is allowed to cool to RT and filtered, washing with DMAc. The filtrate is poured into water (100 ml) and extracted with CH_2Cl_2 (100 ml). The organic phase is collected, washed with brine, dried over Na_2SO_4 and evaporated under reduced pressure. The crude product is purified by dry flash column chromatography (toluene/n-hexane 1:1) followed by column chromatography (eluent: toluene/n-hexane 1:9 -> toluene /n-hexane 1:1). Product (684 mg) is crystallized from MeCN under N_2 (566 mg, 1.65 mmol, yield 43%, m.p.: 133.5-134.2 °C).

^{1}H NMR (500MHz, CD_2Cl_2) δ [ppm]: 8.34 (d, J=7.0 Hz, 2H), 7.37 (d, J=8.9 Hz, 2H), 7,30 (s, 2H), 6,75 (t, J=7.9 Hz, 2H), 6.55 (t, J=6.8 Hz, 2H), 6.28 (bs, 2H), 2.47 (s, 6H)

^{13}C NMR (125.7MHz, CD_2Cl_2) δ [ppm]: 134.04, 133.67, 128.29, 126.28, 123.69, 119.10, 118.38, 116.12, 111.01, 101.94, 13.44.

5. Synthesis of INZ-5

INZ-5 was prepared in two steps through the formation of the 2-methylindolizine-3-carbothialdehyde intermediate:



5.1 Synthesis of 2-methylindolizine-3-carbothialdehyde

In a three-necked flask under N_2 atmosphere, a solution of $POCl_3$ (1.645 g, 25.15 mmol) in anhydrous DMF (20 ml) was dropped over a period of 30 minutes to a solution of 2-methylindolizine (3.000 g, 22.87 mmol) in anhydrous DMF (20 ml) previously cooled to -50°C. The reaction was kept at this temperature for 1 h, then allowed to reach room temperature. The reaction mixture was then poured into a 2 M solution of NaSH in water (150 ml). A red precipitate was formed and filtered off. The raw solid was purified by column chromatography (alumina, eluent: 9:1 hexane:toluene) giving 2-methylindolizine-3-carbothialdehyde as a brown solid (2.627 g, 66%).

^1H NMR δ (CH_2Cl_2): 11.35 (d, 1H, J=6.8), 10.62 (s, 1H), 7.60 (d, 1H, J=8.5), 7.53-7.50 (m, 1H), 7.13-7.10 (m, 1H), 6.53 (s, 1H), 2.55 (s, 3H)

5.2 Synthesis of E-1,2-bis(2-methylindolizin-3-yl)ethene (INZ-5)

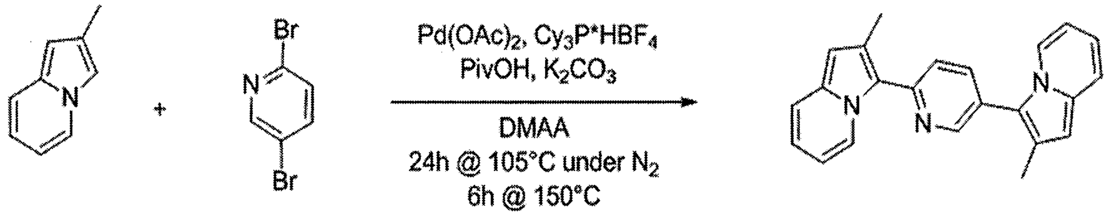
A solution of 2-methylindolizine-3-carbothialdehyde (1.388 g, 7.92 mmol) in anhydrous THF (50 ml) was stirred at r.t. and after the air was replaced by N_2

gas, tributylphosphine (5.768 g, 28.51 mmol) was added. The reaction was kept at reflux temperature till the reagent disappeared (monitored by TLC). The solvent was removed in vacuo, the excess of tributhylphosphine was distilled and E-1,2-bis(2-methylindolizin-3-yl)ethene was purified by filtration on silica gel (eluent: hexane:AcOEt 200:8), yellow powder, yield 28%.

^{1}HNMR δ (C_6D_6): 7.68 (d, 2H, J=7.3), 7.18 (s, 2H), 6.86 (s, 2H), 6.44-6.40 (m, 4H), 6.17-6.14 (m, 2H), 2.44 (s, 6H)

^{13}C NMR δ (C_6D_6): 133.63, 124.97, 122.84, 122.10, 119.34, 117.45, 115.61, 111.08, 103.70, 14.76

6. Synthesis of INZ-6



In a screw-capped glass pressure cylinder (total volume 120 ml) a mixture of K_2CO_3 (3.162 g, 22.88 mmol), 2,5-dibromopyridine (1.719 g, 7.26 mmol), Cy_3P*HBF_4 (213.6 mg, 0.58 mmol), $Pd(OAc)_2$ (65.19 mg, 0.29 mmol) and pivalic acid (445.2 mg, 4.36 mmol) is prepared in air. The tube is transferred in a N_2-filled glove-box and 2-methylindolizine (2.000 g, 15.25 mmol) is added to the mixture followed by 15 ml of anhydrous DMAc. The tube is tightly closed with a Teflon cap and heated to 105°C in an heating bath for 24 h, then the temperature was raised till 150°C for 6 h. The mixture is then allowed to cool to RT, poured in water (150 ml) and extracted with AcOEt (150 ml). The organic phase is collected and dried over $MgSO_4$ and evaporated under reduced pressure. The product has been purified by filtration on silica gel (eluent: hexane gradient hexane:AcOEt 4:1). (yellow powder, 600 mg, yield 24%)

^{1}H NMR δ (C_6D_6) : 9.52 (s, 1H), 8.52 (s, 1H), 7.73 (d, 1H, J=7.1), 7.31 (dd, 1H, J=8.3, J=2.33), 7.26 (d, 1H, J=8.8), 7.18 (d, 2H, J=8.9), 6.54-6.51 (m, 1H), 6.44-6.39 (m, 3H), 6.31-6.28 (m, 1H), 6.07-6.05 (m, 1H), 2.45 (s, 3H), 2.45 (s, 3H)

^{13}CNMR δ (C_6D_6): 151.61, 150.47, 137.19, 135.18, 133.99, 126.91, 126.66, 124.93, 124.37, 123.15, 122.62, 121.70, 120.23, 119.70, 119.51, 118.80, 117.99, 111.02, 110.79, 104.02, 102.55, 15.35, 13.07.

Part B: Polymerization of INZ materials

1. Chemical polymerization of INZ-0

Under N_2 atmosphere, N-methyl-imidazole (1.313 g, 16.00 mmol) and Baytron-CB-40 (21.7 g, 15.2 mmol) were added to a stirred solution of 2-methylindolizine (**INZ-0**, 1.000 g, 7.62 mmol) in dry MeCN (40 ml). The mixture was heated to reflux for 7.5 h, cooled to RT and kept under stirring for 3 days. The precipitate was collected by filtration as a dark solid. Product was sonicated and filtered twice with MeCN. The same procedure was repeated with MeOH (2x50 ml). The product was finally filtered and washed with fresh MeOH followed by Et_2O. Residual solvent was removed under reduced pressure at 40°C. Dark solid (1.160g).

2. Chemical polymerization of INZ-2

Under N_2 atmosphere, N-methyl-imidazole (1.428 g, 17.40 mmol) and Baytron-CB-40 (21.64 g, 15.20 mmol) were added to a stirred solution of 2-phenylindolizine (**INZ-2**, 1.604 g, 8.30 mmol) in dry MeCN (50 ml). The mixture was heated to reflux for 36 h, cooled to RT and kept under stirring for 1 day. The precipitate was collected by filtration as a dark solid. Product was sonicated with MeCN (40 ml) and filtered. The solid was suspended again in MeCN, stirred for 2h and filtered. The obtained product was continuously extracted with MeOH in a Soxhlet apparatus for 24 h. Residual solvent was removed under reduced pressure at 65°C obtaining product as a brown solid (1.425 g).

3. Chemical polymerization of INZ-3

In a dry 2-necked flask, under N2 atmosphere, a mixture of $Fe(OTs)_3$ (3.944 g, 6.93 mmol), N-methylimidazole and INZ-3 (1.000 g, 2.972 mmol) in anhydrous benzonitrile (10 ml) is heated to 145°C for 6 h and stirred at room temperature overnight. The mixture is diluted with MeCN, poured in a cellulose thimble and extracted in a Soxhlet extractor (MeOH (4h), MeCN (8 h), CH_2Cl_2 (8h)). The residue is dried at 50°C under reduced pressure for 8 h (737 mg).

4. Chemical polymerization of INZ-4

In a dry 2-necked flask, under N_2 atmosphere, a mixture of $Fe(OTs)_3$ (9.697 g, 17.03 mmol), and bis(2-methylindolizino)thienylene (2.500 g, 7.30 mmol) in anhydrous benzonitrile (25 ml) is heated to 145°C for 6 h and stirred at room temperature overnight. The mixture is diluted with MeCN, poured in a cellulose thimble and extracted in a Soxhlet extractor (MeOH (10h), MeCN (8 h), CH_2Cl_2 (4h)). The residue is dried at 60°C under reduced pressure for 8h (900 mg).

5. Electrochemical polymerization protocol

Electrochemical polymerization was carried out by cyclic voltammetry. The monomer was dissolved (5 mM) in an electrolyte solution made by 0.1 M

$TBAClO_4$ in ACN. 15 CV cycles between -0.2 and 1.0 V vs. RE were performed in a three-electrode two-compartment cell assembled using:

- a 1 cm^2 (each face) carbon cloth working electrode
- a Pt mesh counter electrode (in the separated compartment)
- a Ag/AgCl wire as RE (+3.1 V vs. Li).

Examples of electrochemical polymerization process for INZ-0, INZ-2, INZ-3, INZ-4, and INZ-5 are reported in Figure 5 (a), (b), (c), (d), and (e), respectively.

Part C: Electrochemical characterization

As a state-of-the-art performance of an organic species known for its use as an energy storage materials at a cathode, reference may be made to the performance of the TEMPO organic radical – see in this respect Figure 3 (adapted from ECS Interface, Winter 2005, p34). As shown, this state-of-the-art material has electrochemical activity close to 3.5 V vs. Li^+/Li.

In the present invention, the synthesized molecules INZ-0, INZ-2, INZ-3, INZ-4 and INZ-5 were electropolymerized (Figure 5) and the resulting layers tested for their electrochemical activity. Cyclic Voltammetries (CVs) were performed in monomer free, 0.1 $LiClO_4$ propylene carbonate solution at 50 mV/s in flooded cell using metallic lithium foils as both reference and counter electrodes. The resulting current potential profiles for layers obtained from INZ-0, INZ-2, INZ-3, INZ-4, and INZ-5 are reported in Figure 6 (a), (b), (c), (d), and (e), respectively. An example of battery performances obtained using the layer obtained by INZ-5 and metallic lithium as positive and negative electrodes is reported in Figure 7. The battery was assembled using a 1 M $LiPF_6$ EC/DMC commercial electrolyte in a Swagelock cell.

As shown by the data shown in the Figures, it is clear that the indolizine electrochemical activity occurs above 3.8V vs. Li^+/Li. This represents a 10% increase over the state-of-the-art.

"Metal-free" batteries were prepared as follows: To prepare the positive electrode, INZ-4 was mixed with carbon (Super P) and binder (styrene-butadiene rubber and carboxymethyl cellulose) in a 60:30:10 wt% proportion. Water was added to the mixture until a homogeneous slurry was obtained. Similarly, to prepare the negative electrode, NPbIm-1 was mixed with carbon (Super P) and binder (styrene-butadiene rubber and carboxymethyl cellulose) in a 75:15:10 wt% proportion. Water was added to the mixture until a homogeneous slurry was obtained. Both slurries were then cast on aluminum foil with the Doctor Blade method. The as-cast electrodes were then dried at 80°C in air overnight. Test electrodes were cut from the dried sheet in the form of circles with a diameter of 16mm. A "metal-free" electrolyte was prepared as follows: tetrabutylammonium perchlorate was added to acetonitrile to form a 1M solution. The solution is stable at room temperature. Coin-cell type batteries were assembled from the prepared parts. A negative electrode sample was placed as anode material, covered with a glass fiber separator, and the separator was flooded with 250µl of the electrolyte solution. A positive electrode was placed on top of the separator, and the cell was sealed by crimping. The as-prepared coin cell was cycled in a constant-current constant-voltage pattern (CCCV) using a current of 10µA/mg in the potential interval 0.1V – 2.5V. The cells were placed in a temperature chamber and kept at 25°C throughout the experiment. A typical charge-discharge curve for the "metal-free" battery is shown in Figure 8.

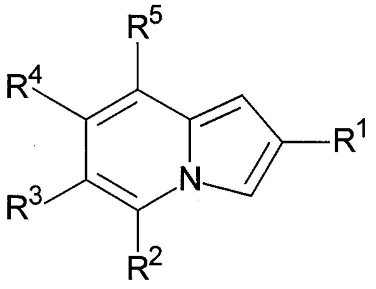
Claims

1. A battery comprising a positive electrode, a negative electrode and an electrolyte therebetween, wherein either the positive electrode or the negative electrode contains an indolizine-based material.

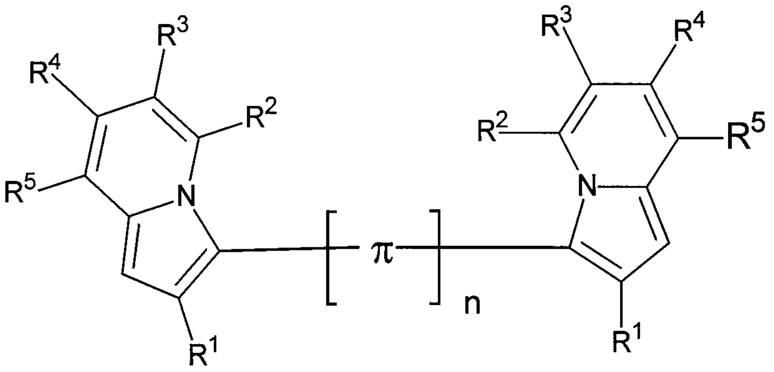
2. A battery according to claim 1, wherein the positive electrode contains an indolizine-based material.

3. A battery according to claim 1 or 2, wherein the positive electrode or the negative electrode contains at least 50 % by mass of the indolizine-based material.

4. A battery according to any of claims 1 to 3, wherein the indolizine-based material contains one of the following compounds and/or is obtained by polymerization of one or more compounds according to formula (I) and/or (II) below:



(I)



(II)

wherein:

R^1 can be a hydrogen atom or any linear or branched alkyl chain, or glycolic chain, having from 1 to 8 carbon atoms, an ester whose alcoholic residue is an alkyl chain which is linear or branched having up to 8 carbons / an ester having up to 10 carbon atoms in all, a benzene ring, or a naphthalene ring substituted at the 1 or 2 position;

R^2, R^3, R^4, and R^5 may be H, methyl, branched or linear alkyl chains up to 8 carbon atoms, halogens, esters and amides preferably with 8 or less carbon atoms, alkyl and aryl nitriles preferably with 8 or less carbon atoms, nitro derivatives, sulfones and sulfoxides, perfluoroalkyl preferably with 8 or less carbon atoms, alkoxy groups preferably with 8 or less carbon atoms, dialkylamino preferably with 8 or less carbon atoms, diarylamino, phenyl, 1-naphthyl, 2-naphthyl;

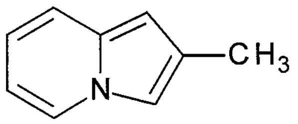
π in formula (II) may be a double bond, a triple bond, or a plurality of double or triple bonds conjugated in a number of 2 or 3, such as a benzenic ring, a thiophenic ring, a furane ring or a pyridine ring, such rings being optionally substituted by substituents as defined for R^2 to R^5, and n in formula (II) is an integer of at least 1, and is preferably equal to 1.

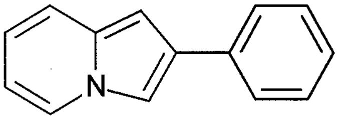
5. A battery according to claim 4, wherein a compound of formula (I) or (II) is used wherein R^1 is Me or C_6H_5.

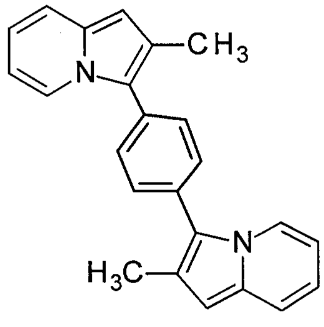
6. A battery according to claim 5, wherein a compound of formula (I) or (II) is used wherein R^1 is Me.

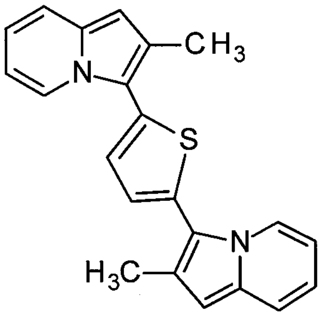
7. A battery according to any of claims 4 to 6, wherein a compound of formula (II) is used wherein π is -CH=CH-, $-C_6H_4-$, or 2,5-thienyl.

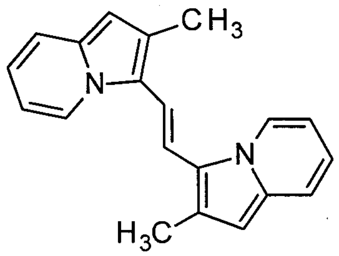
8. A battery according to any of claims 1 to 7, wherein the indolizine-based material is obtained by polymerization of one or more of the compounds having the following structures:





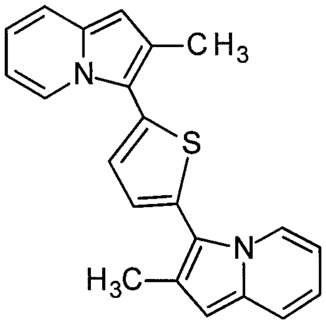






9. Use an indolizine-based material as an energy storage material in an electrochemical energy storage device.

10. Compound having the following formula:



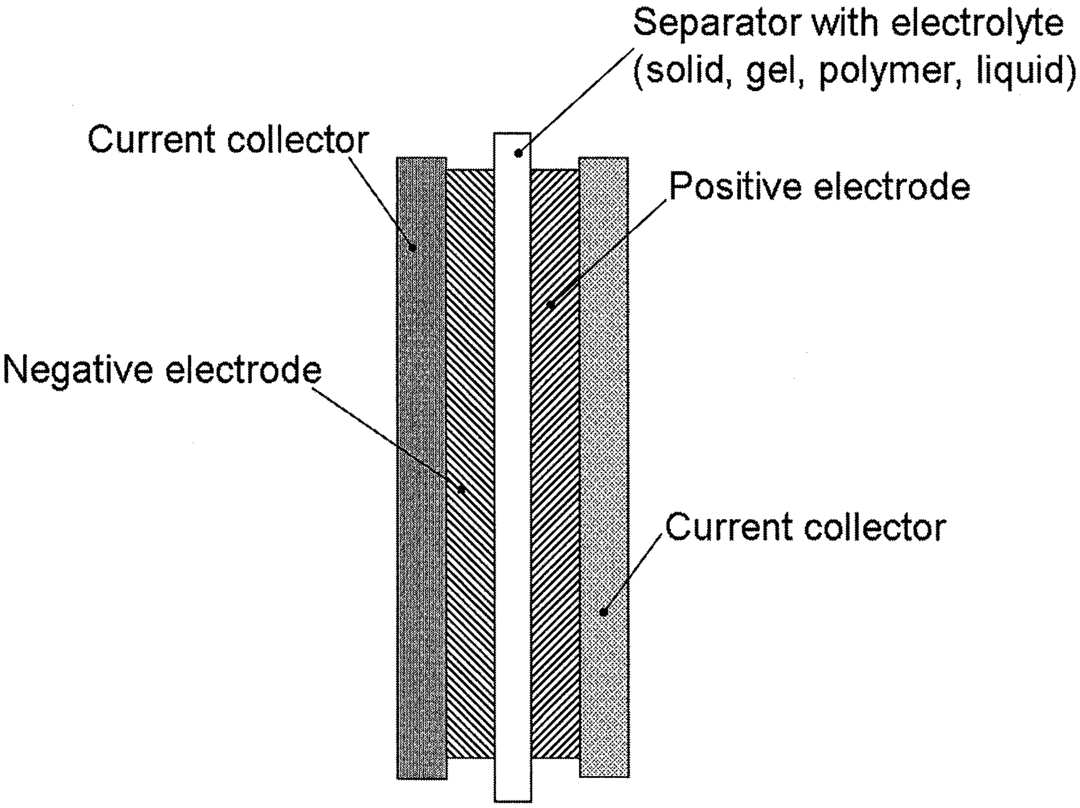
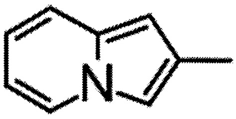
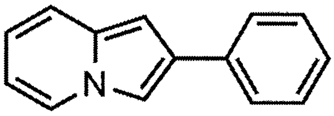

Separator with electrolyte
(solid, gel, polymer, liquid)
Current collector
Positive electrode
Negative electrode
Current collector

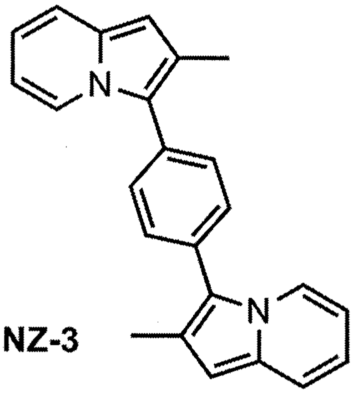
Figure 1



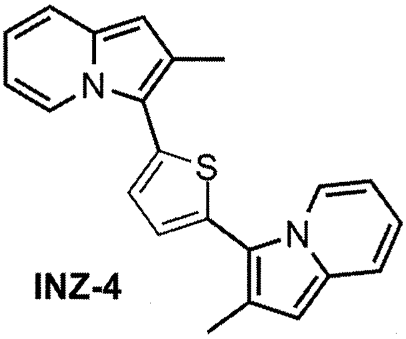
INZ-0



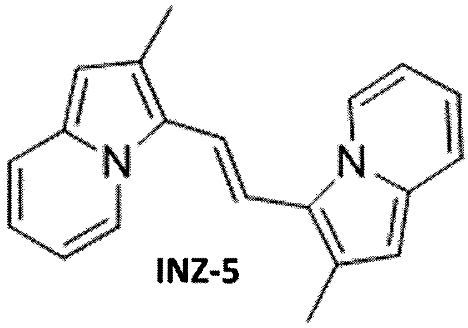
INZ-2



INZ-3



INZ-4



INZ-5

Figure 2

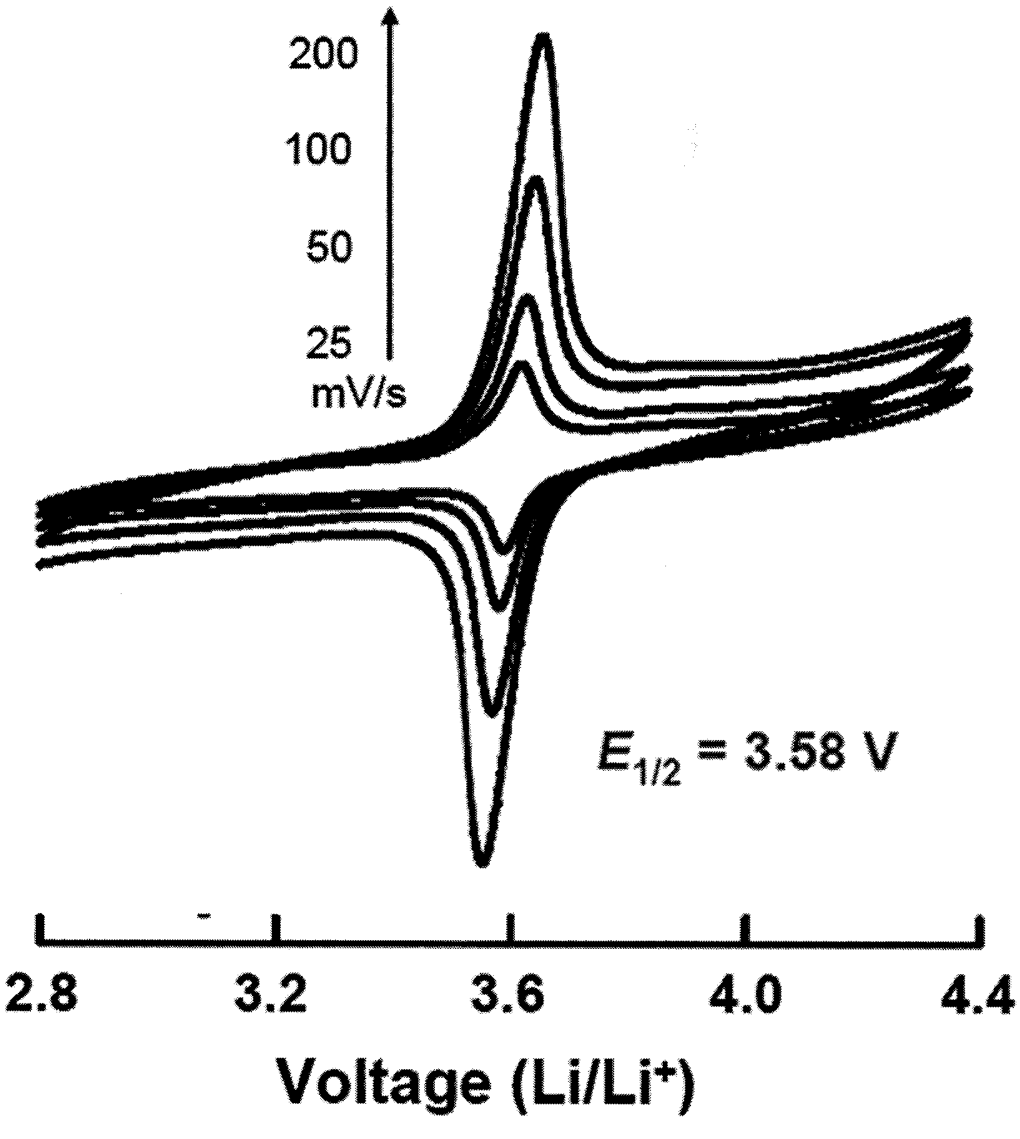


Figure 3

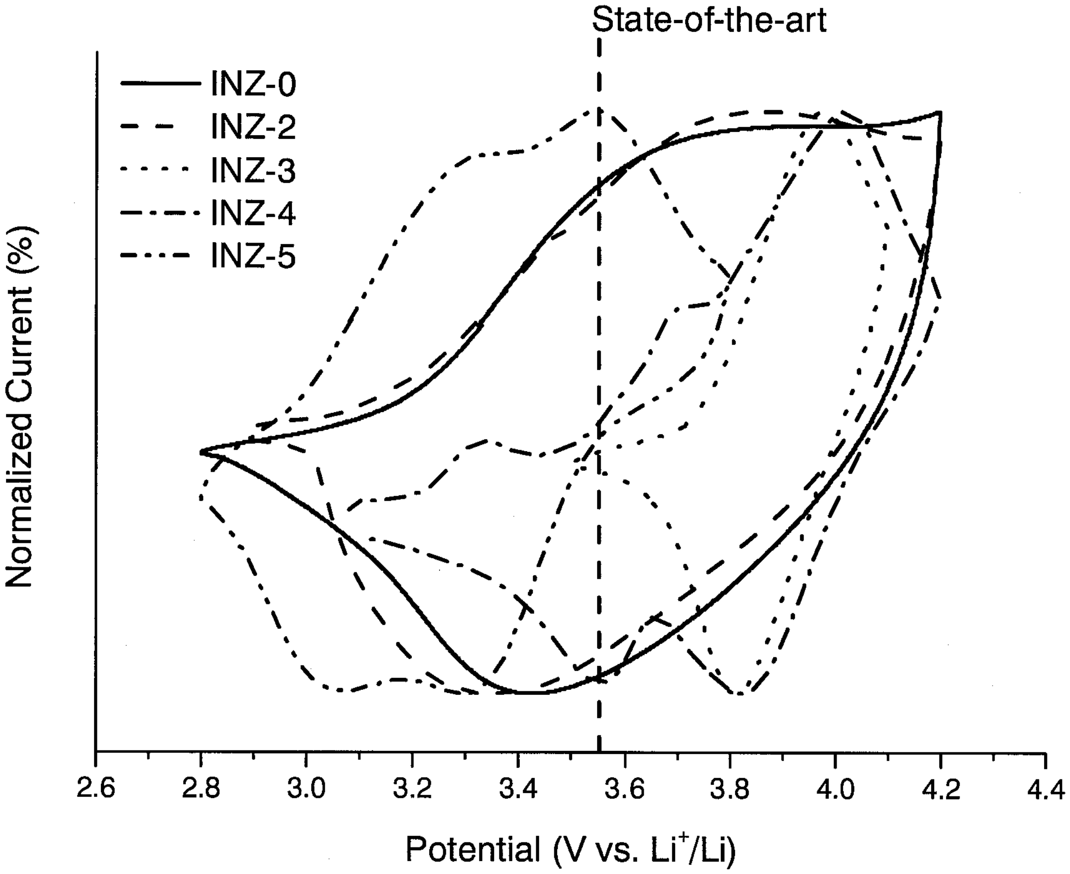

State-of-the-art
INZ-0
INZ-2
INZ-3
INZ-4
INZ-5
Normalized Current (%)
Potential (V vs. Li$^+$/Li)
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4

Figure 4

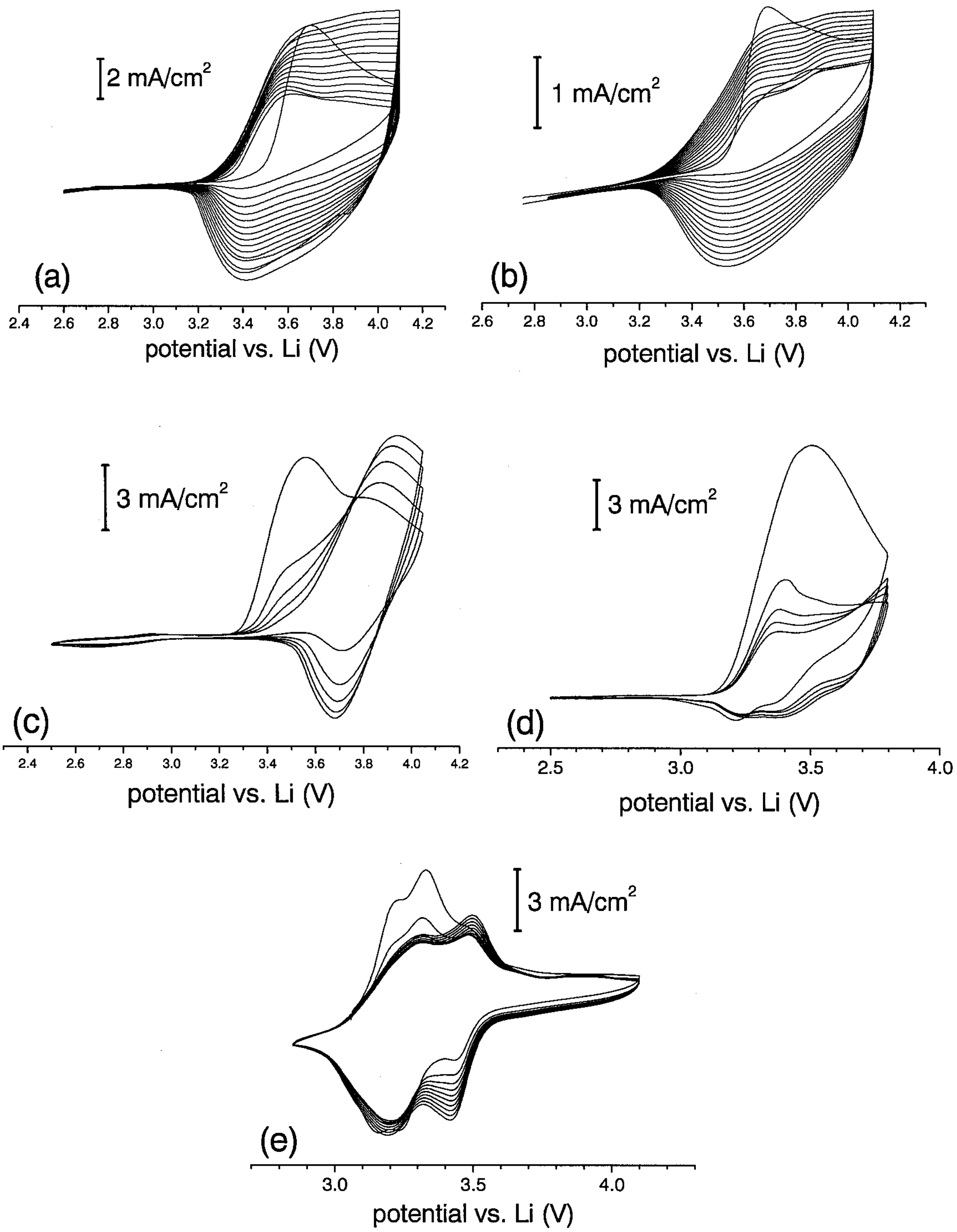

2 mA/cm²
(a)
2.4 2.6 2.8 3.0 3.2 3.4 3.6 3.8 4.0 4.2
potential vs. Li (V)
1 mA/cm²
(b)
2.6 2.8 3.0 3.2 3.4 3.6 3.8 4.0 4.2
potential vs. Li (V)
3 mA/cm²
(c)
2.4 2.6 2.8 3.0 3.2 3.4 3.6 3.8 4.0 4.2
potential vs. Li (V)
3 mA/cm²
(d)
2.5 3.0 3.5 4.0
potential vs. Li (V)
3 mA/cm²
(e)
3.0 3.5 4.0
potential vs. Li (V)

Figure 5

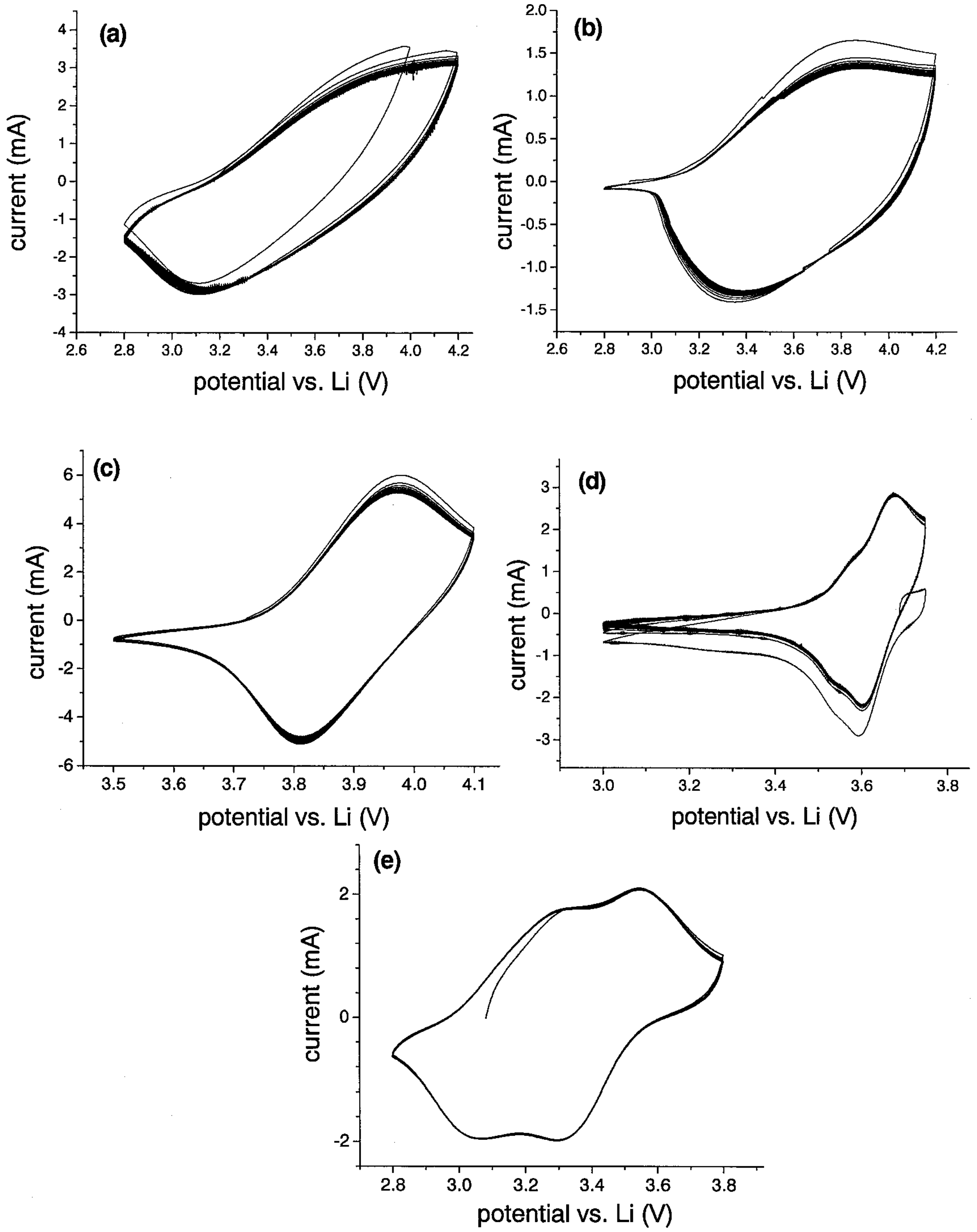

(a)
current (mA)
4
3
2
1
0
-1
-2
-3
-4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
potential vs. Li (V)
(b)
current (mA)
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
potential vs. Li (V)
(c)
current (mA)
6
4
2
0
-2
-4
-6
3.5
3.6
3.7
3.8
3.9
4.0
4.1
potential vs. Li (V)
(d)
current (mA)
3
2
1
0
-1
-2
-3
3.0
3.2
3.4
3.6
3.8
potential vs. Li (V)
(e)
current (mA)
2
0
-2
2.8
3.0
3.2
3.4
3.6
3.8
potential vs. Li (V)

Figure 6

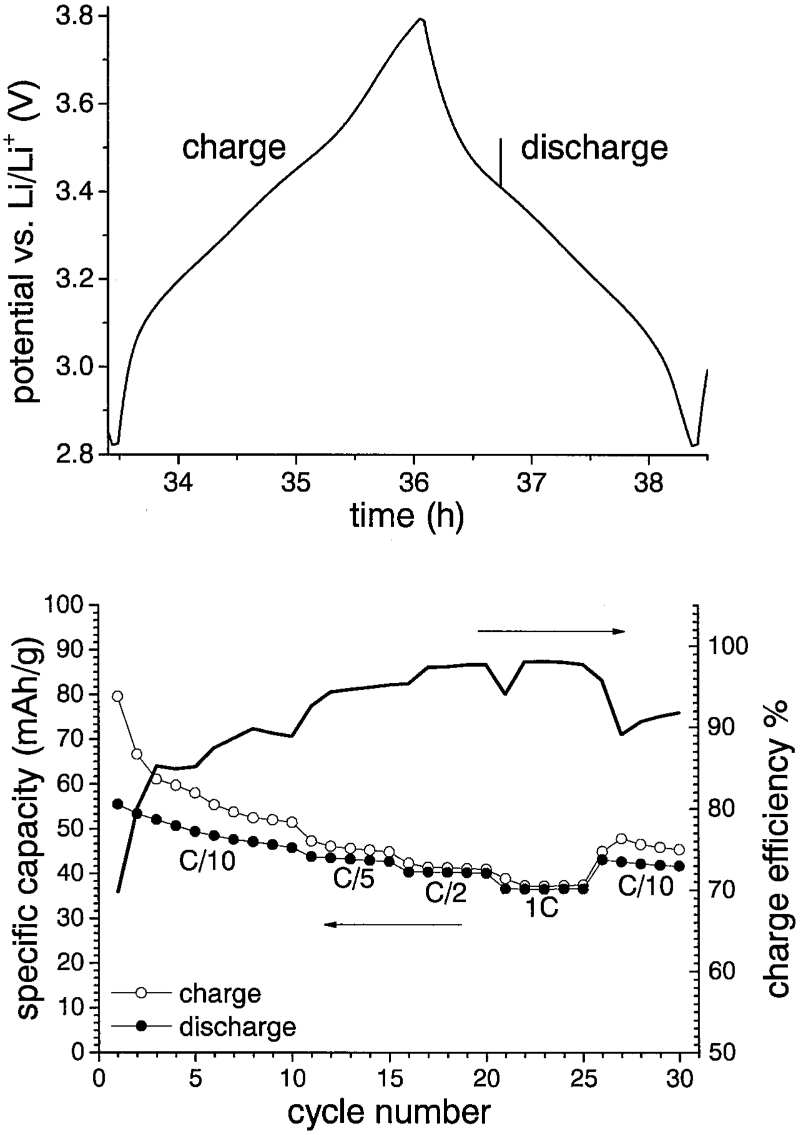

potential vs. Li/Li$^+$ (V)
3.8
3.6
3.4
3.2
3.0
2.8
charge
discharge
34
35
36
37
38
time (h)
specific capacity (mAh/g)
100
90
80
70
60
50
40
30
20
10
0
charge efficiency %
100
90
80
70
60
50
C/10
C/5
C/2
1C
C/10
charge
discharge
0
5
10
15
20
25
30
cycle number

Figure 7

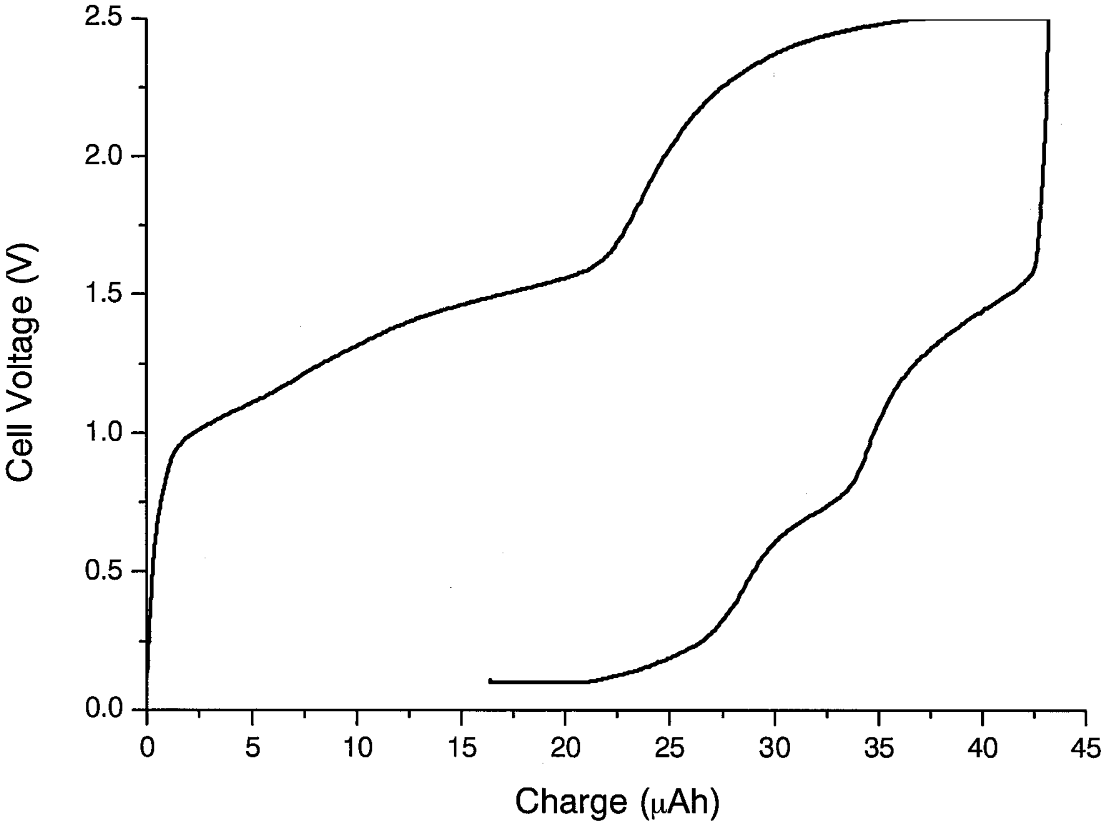

Cell Voltage (V)
0.0
0.5
1.0
1.5
2.0
2.5
Charge (μAh)
0
5
10
15
20
25
30
35
40
45

Figure 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2013/076398

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☒ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2013/076398

A. CLASSIFICATION OF SUBJECT MATTER

INV. H01M4/60 H01M10/0525 H01M10/36 C07D519/00

ADD. H01M4/36

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)

H01M C07D

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2008/047324 A2 (HIGH POWER LITHIUM S A [CH]; EXNAR IVAN [CH]; ZAKEERUDDIN SHAIK MOHAMM) 24 April 2008 (2008-04-24) page 4, paragraph 2 page 5, paragraph 3 - paragraph 5 page 7, paragraph 3 -----	1-6,9
X	DE 39 29 383 A1 (BASF AG [DE]) 7 March 1991 (1991-03-07)	1-9
A	page 2, line 18 - line 22 page 2, line 51 - page 3, line 11 page 4, line 47 - line 55 -----	10
A	EP 1 215 745 A1 (MATSUSHITA ELECTRIC IND CO LTD [JP]) 19 June 2002 (2002-06-19) paragraphs [0015], [0031] - [0036] ----- -/--	1-9

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

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"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

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search 17 April 2014	Date of mailing of the international search report 02/05/2014
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Gomes Pinto F., R

1

International application No
PCT/EP2013/076398

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	N. P. BUU-HOÏ ET AL: "Nitrogen heterocyclic analogs of polyaryls", JOURNAL OF HETEROCYCLIC CHEMISTRY, vol. 2, no. 1, 1 March 1965 (1965-03-01), pages 7-10, XP055012225, ISSN: 0022-152X, DOI: 10.1002/jhet.5570020102 compounds 19, 20 -----	9,10

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2013/076398

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2008047324 A2	24-04-2008	AT 548765 T	15-03-2012
		EP 2084774 A2	05-08-2009
		JP 2010507210 A	04-03-2010
		KR 20090091124 A	26-08-2009
		US 2010068621 A1	18-03-2010
		WO 2008047324 A2	24-04-2008
DE 3929383 A1	07-03-1991	NONE	
EP 1215745 A1	19-06-2002	CN 1349672 A	15-05-2002
		EP 1215745 A1	19-06-2002
		JP 4411691 B2	10-02-2010
		JP 2001015158 A	19-01-2001
		KR 20070037749 A	06-04-2007
		US 2008014496 A1	17-01-2008
		WO 0103226 A1	11-01-2001

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-10

battery comprising indolizine based material and use of indolizine based material in an electrochemical energy storage device

1.1. claim: 10

indolizine compound
