



US 20030118877A1

(19) **United States**

(12) **Patent Application Publication**
Armand et al.

(10) **Pub. No.: US 2003/0118877 A1**

(43) **Pub. Date: Jun. 26, 2003**

(54) **NEW ELECTRODE MATERIALS DERIVED FROM POLYQUINONIC IONIC COMPOUNDS AND THEIR USE IN ELECTROCHEMICAL GENERATORS**

(76) Inventors: **Michel Armand**, Montreal (CA);
Christophe Michot, Grenoble (FR);
Nathalie Ravet, Montreal (CA)

Correspondence Address:
PATENT ADMINSTRATOR
KATTEN MUCHIN ZAVIS ROSENMAN
525 WEST MONROE STREET
SUITE 1600
CHICAGO, IL 60661-3693 (US)

(21) Appl. No.: **10/288,575**
(22) Filed: **Nov. 6, 2002**

Related U.S. Application Data

(60) Division of application No. 09/361,962, filed on Jul. 28, 1999, which is a continuation of application No. PCT/CA98/01125, filed on Dec. 2, 1998.

(30) **Foreign Application Priority Data**

Dec. 2, 1997 (CA) 2,223,562

Publication Classification

(51) **Int. Cl.⁷** **H01M 8/00**
(52) **U.S. Cl.** **429/12; 429/209; 526/259**

(57) **ABSTRACT**

The present invention is concerned with novel compounds derived from polyquinonic ionic compounds and their use in electrochemical generators.

NEW ELECTRODE MATERIALS DERIVED FROM POLYQUINONIC IONIC COMPOUNDS AND THEIR USE IN ELECTROCHEMICAL GENERATORS

FIELD OF THE INVENTION

[0001] The present invention is concerned with novel polyquinonic ionic compounds useful as electrode materials used for example in electrochemical generators.

BACKGROUND OF THE INVENTION

[0002] Electrode materials derived from transition metals, in particular transition metals binary chalcogenides, such as TiS_2 , VO_x ($2 \leq x \leq 2.5$), ternary oxides such as LiNiO_2 , LiCoO_2 , $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ ($0 \leq x \leq 1$), et LiV_3O_8 , are known. These materials are however often relatively toxic. With the exception of vanadium derivatives, the capacities are practically modest, i.e. on the order of 100 Ah.g^{-1} , and their potential (about 4 V vs $\text{Li}^+/\text{Li}^\circ$) are beyond the domain of stability of solid or liquid electrolytes. They are therefore problematic in terms of safety.

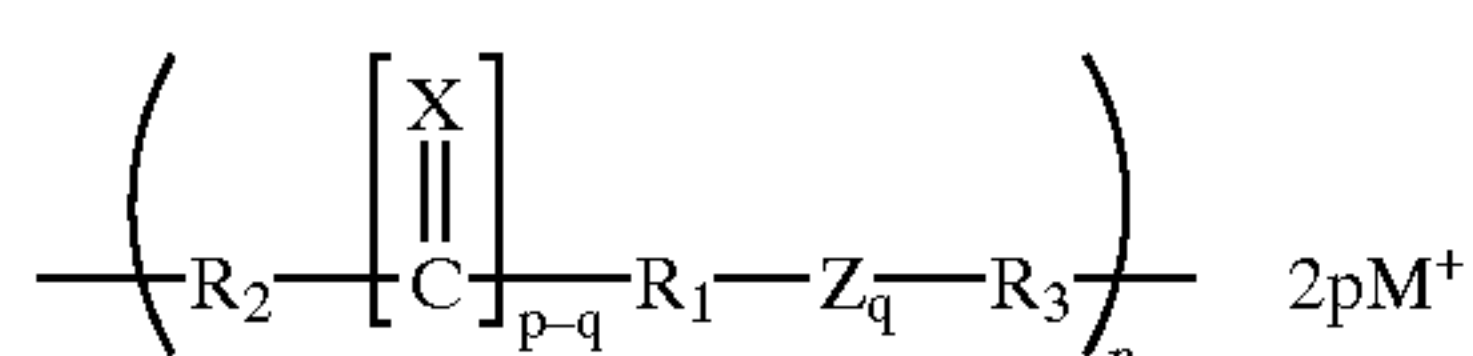
[0003] Organic compounds like conjugated polymers work through an insertion mechanism of anions taken from the electrolyte. The mass capacities resulting therefrom are consequently low and the cycling possibilities are disappointing.

[0004] Other known compounds are those of the polydisulfide type, which, even if they do not have intrinsic electronic conductivity, possess interesting redox properties and mass capacities ($\geq 300 \text{ Ah.g}^{-1}$), particularly oxidizing coupling derivatives of 2,5-dimercaptothiadiazole. However, the resulting reduction products and intermediates are lithium salts like conjugated thiolates with a nitrogen atom. Delocalization of the charge on the polarisable anionic centers like sulfur and nitrogen, lead to a relatively important solubility in the electrolytes, as well as a reduced cycling life span.

[0005] Monoquinones are organic compounds known for their redox properties, but the potentials are of little interest (on the order of 2.2 V vs. $\text{Li}^+/\text{Li}^\circ$), and the neutral oxidized compounds are soluble in the electrolytes. Polymers bearing quinonic functions such as those resulting from hydroquinone and formaldehyde polycondensation, are not electrochemically active because of the reduced mobility of the charge carriers, ions and electrons, in the absence of highly polar protic solvents like water.

SUMMARY OF THE INVENTION

[0006] The present invention concerns electroactive compounds derived from anion salts bearing at least 2 quinone functions cumulated, conjugated, or both, in the same molecule. More specifically, the invention comprises a redox compound having at least one state of oxidation state represented by the general formula:



[0007] wherein

[0008] M^+ represents an alkaline metallic cation, an alkaline-earth cation, a transition metal cation, a rare earth cation, an organometallic cation, an organic cation of the "nium" type, a repetitive unit of a cationic oxidized conjugated polymer, or a monomeric or polymeric cation optionally having a redox character;

[0009] X is oxygen, NCN, or $\text{C}(\text{CN})_2$;

[0010] Z is $\text{C}-\text{Y}^-$ or N^- ;

[0011] Y represents oxygen, sulfur, NCN, $-\text{C}(\text{CN})_2$, with the proviso that when Y is sulfur and n is ≤ 4 , then X is oxygen;

[0012] R_1 is absent, O, S, NH, $-(\text{C}=\text{C})_r-$, $-(\text{W}=\text{W})_r-$ wherein W is independently CR^6 or N; r varies between 1 and 12; and R^6 is H, halogen, CN, or C_{1-12} alkyl, C_{2-12} alkenyl or C_{6-14} aryl optionally having one or more substituents oxa, aza or thia; and wherein 2 R^6 groups can be bonded to form a cycle comprising from 3 to 7 members;

[0013] R^2 and R^3 are the same or different and are absent, a carbonated divalent radical, optionally substituted with aza, oxa or thia;

[0014] q varies between 0 et p;

[0015] p varies between 1 and 5;

[0016] n varies between 1 and 10^4 ; and

[0017] wherein two of R^1 , R^2 and R^3 can be bonded together to form a cycle comprising 3 to 7 members.

[0018] For the purposes of the present invention, when n is 4 or less, the compound of the invention is not considered a polymer. In addition, the expression "divalent radical" is defined as an alkylene, an arylene, or an arylalkylene of from 2 to 200 carbon atoms, and optionally comprising one or more substituents aza, oxa or thia.

[0019] The present application further concerns an electrode material characterized in that it contains, in whole or in part, a compound of the invention, and an electrical energy storage system such as a primary or secondary generator or a super capacity comprising an electrolyte, at least one negative electrode and at least one positive electrode comprising a compound of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0020] In the present invention, a new family of electroactive compounds derived from anion salts bearing a plurality of quinone functions cumulated and/or conjugated in the same molecule is described and claimed. It has been found that such type of compounds have a high capacity, i.e. equal or higher than 300 Ah.g^{-1} , obtained at potentials comprised between 3.5 et 1 V vs. $\text{Li}^+/\text{Li}^\circ$, thus in the domain of stability of conventional aprotic electrolytes, liquid or solid, and allowing the making of positive and negative electrodes for generators. Further, the corresponding salts do not, whatever their degree of oxidation, solubilize significantly in liquid electrolytes or aprotic polymers. The kinetic of the redox reaction in solid phase is noticeable and comparable to that of inorganic insertion materials. It has

also been found that by replacing the oxygen atom of the neutral quinonic groups CO with NCN groups or $C(CN)_2$, and/or the replacement of the oxygen atom of the quinonic groups negatively charged with anionic groups N^- , NCN^- or $C(CN)_2^-$ had the same interesting properties in terms of the redox activity. The redox potential is displaced of about 300 mV towards the positive values by replacing a neutral quinonic oxygen with an NCN or $C(CN)_2$. The chemical methods to perform these substitutions on the quinonic groups are well known to anyone of ordinary skill in the art.

[0021] The redox compounds of the present invention include also polyquinones wherein the negatively charged oxygen of the quinonic groups is replaced with sulfur S^- . In this case, charge conjugation with an oxygenated group CO neutral and weakly polarisable and more electronegative, significantly lowers the solubility of the corresponding ionic derivatives, in particular in electrolytic solutions. An additional degree of oxidation is then obtained by oxidative duplication of CS^- groups to form disulfide bridges $CS-SC$.

[0022] These polyquinonic compounds can also be part of the polymers into which the charges are conjugated along the polymeric chain. In such a case, the solubility of these rigid macromolecules is null, whatever the charge borne by the polymer, thus including the neutral state.

[0023] Because the compounds of the present invention are anion salts, i.e., negatively charged, it is necessary to combine them with a cation in order to have a global neutral charge. The preferred cations comprise the proton, alkaline cations like Li, Na, K, Cs; alkaline-earth cations like Mg, Ca, Ba; transition metal cations like Cu, Zn, Pb, Fe, Ni, Co, Mn, V, Cr; rare earth cations; organometallic cations like metallocenium; cations of the $\llbracket \text{ium} \rrbracket$ type such as ammonium, amidinium, guanidinium, pyridinium, imidazolium, triazolium, imidazolinium, sulfonium, phosphonium, iodonium; a repetitive unit of an oxidized cationic conjugated polymer such as polypyrrole, polythiophene, polyquinolines; cations in the form of monomers or polymers optionally having a redox character such as viologenes of formula $[(R''NC_5H_4-C_5H_4N-)^{2+}]_n$ wherein R'' comprises C_{2-12} alkylene, C_{6-14} arylene or C_{6-14} arylene C_{2-12} alkylene, each optionally substituted with oxa, aza ou thia. The lithium cation and the proton are particularly preferred. Other ions can be present in the electrolytic medium and/or in the electrode material, and can contribute to improve the conductivity of the interfacial properties. The potassium ion is advantageously used in such instance, as well as cations derived from quaternized imidazolium.

[0024] To the redox capacity of the molecules of the present invention can be added that of the cation when the latter possesses many degrees of oxidation. Cations of iron, copper or manganese, as well as metallocenes, are particularly interesting for such application. Organic cations with redox properties, such as viologenes, are similarly useful. These cations can optionally be part of a polymeric chain.

[0025] The compounds of the present invention possess high specific capacities of redox exchange, and in fact superior to those of conventional inorganic compounds. The great variety of functional groups available allows choosing redox potentials in a wide range of potentials, typically between 0.1 to 3.7 V vs. Li^+/Li° . Compounds with redox couples comprised between 0.1 and 2 V vs. Li^+/Li° are

advantageously used as a component of negative electrodes in electrochemical generators of primary and secondary type batteries or supercapacitor. Similarly, compounds with redox couples comprised between 2 and 3.7 V vs. Li^+/Li° are advantageously used as component of positive electrodes in same devices or as an active or passive electrode in electrochromic devices.

[0026] The compounds of the present invention can be used alone or in mixtures thereof. They can also be used in conjunction with other redox compounds, in particular insertion compounds. Such insertion compounds include, for negative electrodes, metallic lithium or alloys thereof, optionally in the form of a nanometric dispersion in lithium oxide; double nitrides of lithium and a metal of transition such as cobalt; oxides with a low potential of general formula $Li_{1+y}Ti_{2-x/4}O_4$ wherein x and y vary between 0 et 1; and carbon and carbonated products resulting from the pyrolysis of organic matters. For the positive electrodes, the insertion compounds include oxides and sulfides of transition metals, such as VO_z wherein z varies between 2 and 2.5; LiV_3O_8 ; $Li_aN_{1-a}Co_aO_2$ wherein a varies between 0 et 1; manganese spinels $Li_yMn_{2-x}M_xO_4$ wherein x varies between 0 and 0.5 and y varies between 0 and 2, and M is Li, Cr, Al, V, Ni; organic polydisulfides; FeS ; FeS_2 ; iron sulfate; iron and lithium phosphates and phosphosilicates of the olivine structure; or the substitution product of iron with manganese, either used alone or in mixtures.

[0027] The materials of the invention are particularly embodied in composite electrodes containing the novel redox compounds, alone or in mixtures, at least one electronic conductor, and at least one polymeric binder. The electronic conductors are preferably selected from carbonated compounds such as carbon black, graphite powder, products resulting from the pyrolysis of organic matters, in particular phenolic resins or polyacrylonitrile. When the electrode binder does not have any electrochemical function but only a mechanical function, the latter is advantageously chosen from non-polar polymers like polytetrafluoroethylene, co- or ter-polymer of ethylene, propylene and a diene, that allow the binding of the materials while leaving a porosity sufficient to permit the required electrolyte penetration for proper operation of these redox materials.

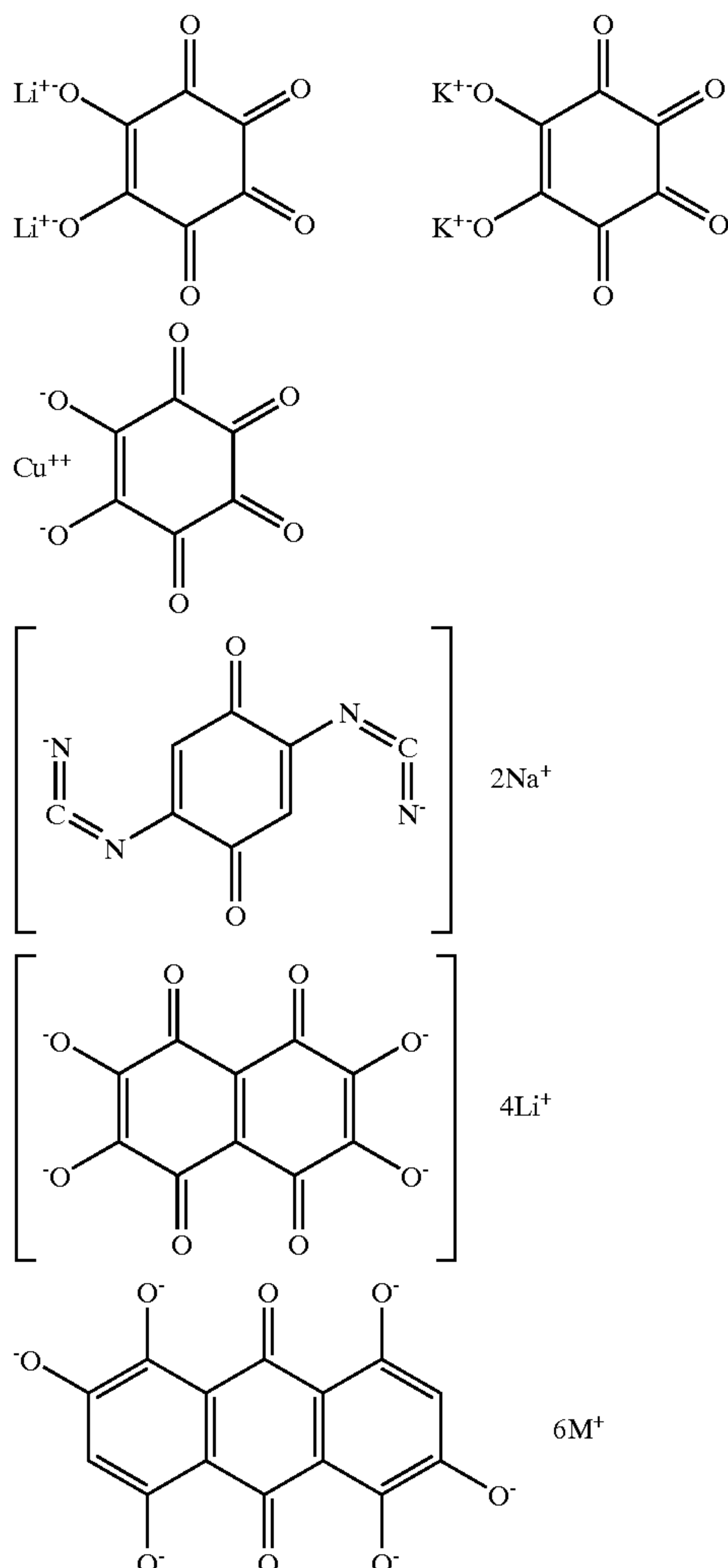
[0028] Liquid electrolytes suitable with such type of redox materials are those obtained by dissolving a salt or an acid in a solvent. The solvents are preferably chosen from cyclic or acyclic carbonates, γ -butyrolactone, monoalkylamides and di-alkylamides, tetraalkylsulfamides, dialkylated ethers of mono, di, tri and tetraethylene glycols, as well as oligomers having a mass lower than 2000 g/mole, and their mixtures.

[0029] In a variation, the electrode binder has an ionic conductivity and allows the maintenance of an intimate contact between the particles of the redox materials in the electrolyte while compensating, because of their plastic or elastomeric character, for the variations of volume inherent to the operation of the electrode. In preferred embodiments, the electrolyte contains, individually or in a mixture, a polar-type polymer, a polar solvent, and/or at least one ionic salt. The polar-type polymers useful with the addition of a liquid solvent are preferably selected from vinylidene fluoride-based homo- or copolymers, acrylonitrile-based homo- or copolymers, methyl methacrylate-based homo- or copoly-

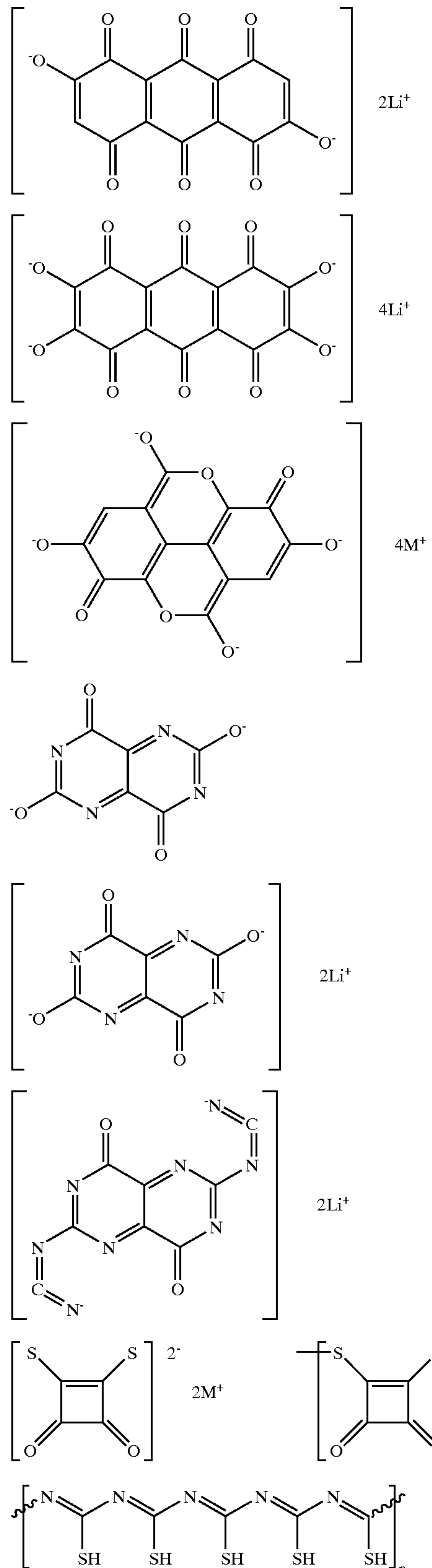
mers. The polar-type polymers useful with or without the addition of a liquid solvent are preferably selected from polyethers such as ethylene oxide-based or propylene oxide-based homo- or copolymers. In a variation of the preferred embodiment of the compounds of the invention, ceramic or cross-linked particles are added to the polymer electrolytes, to improve the mechanical properties.

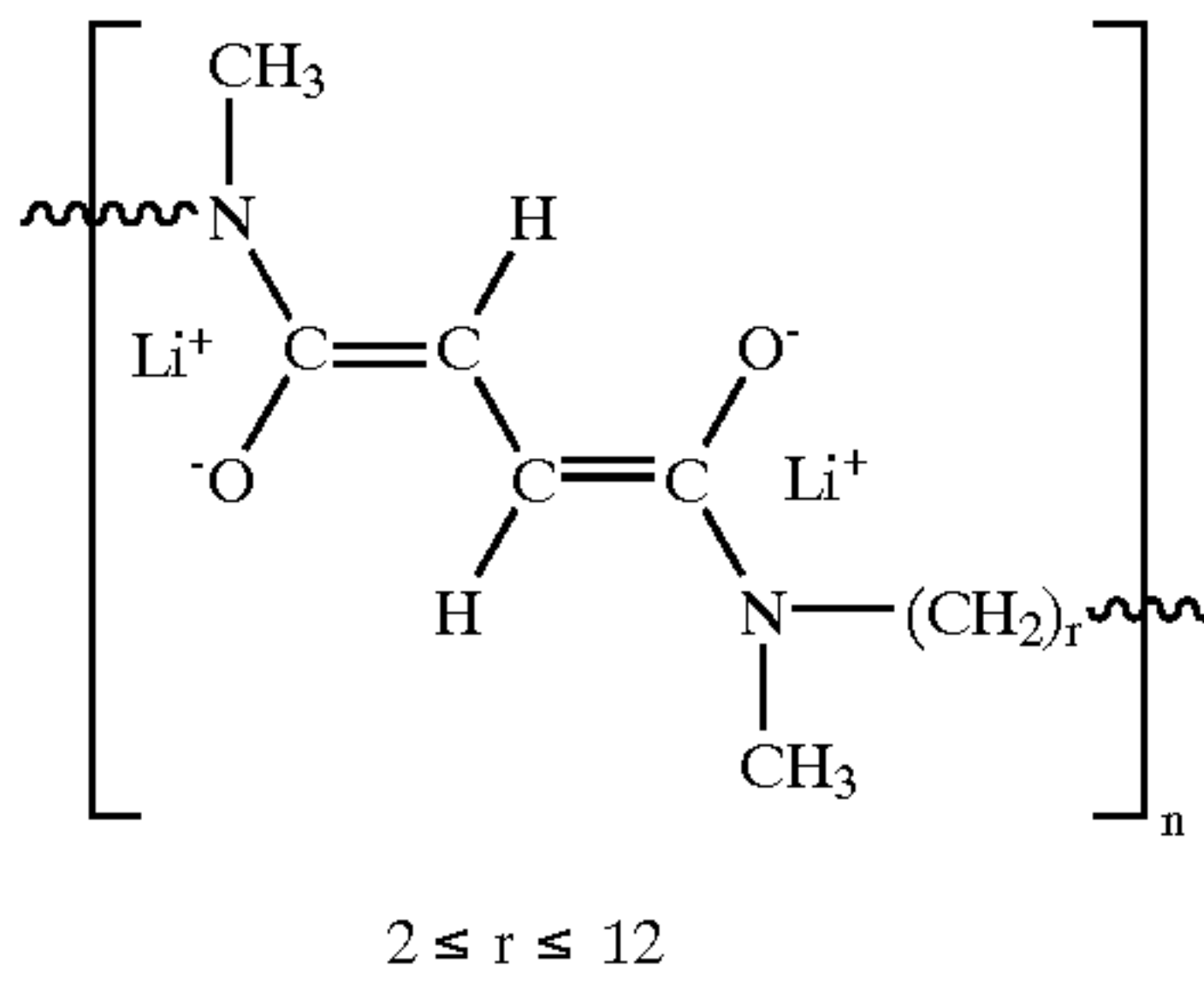
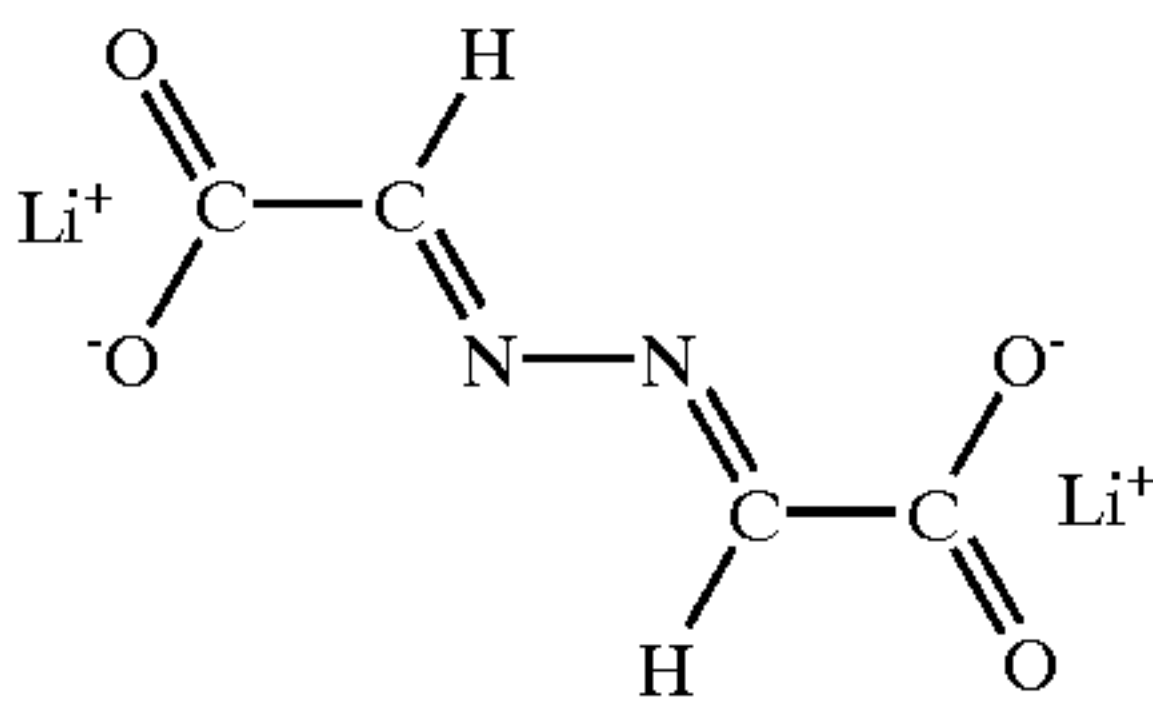
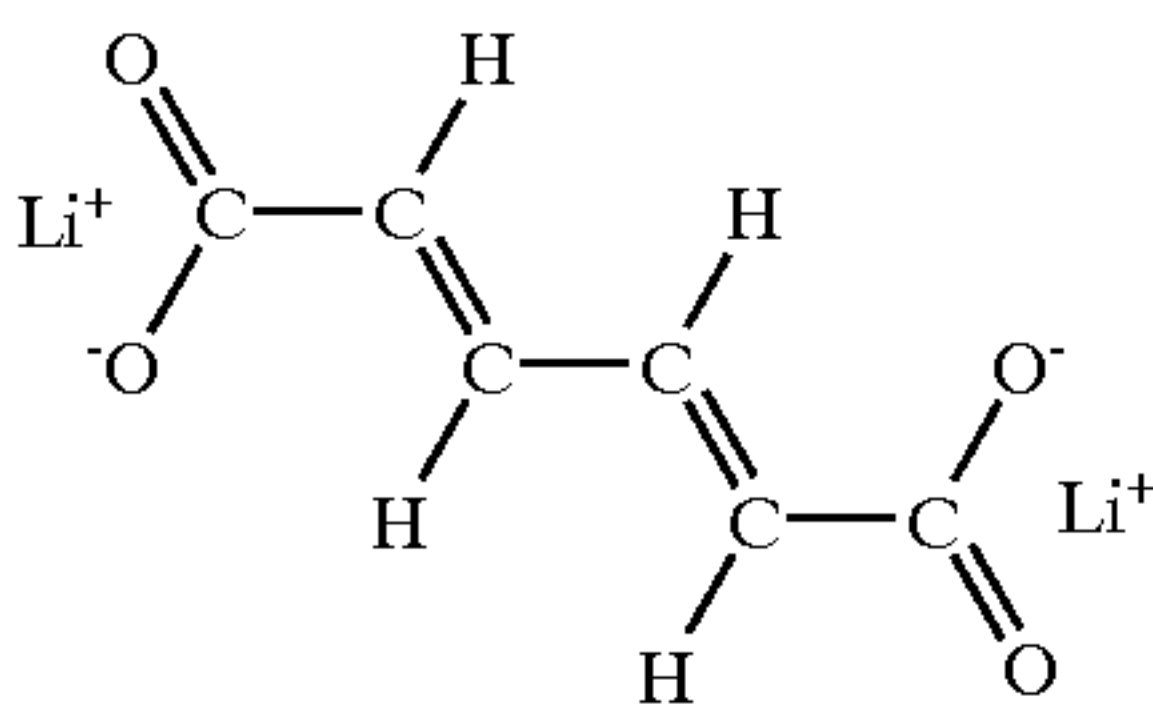
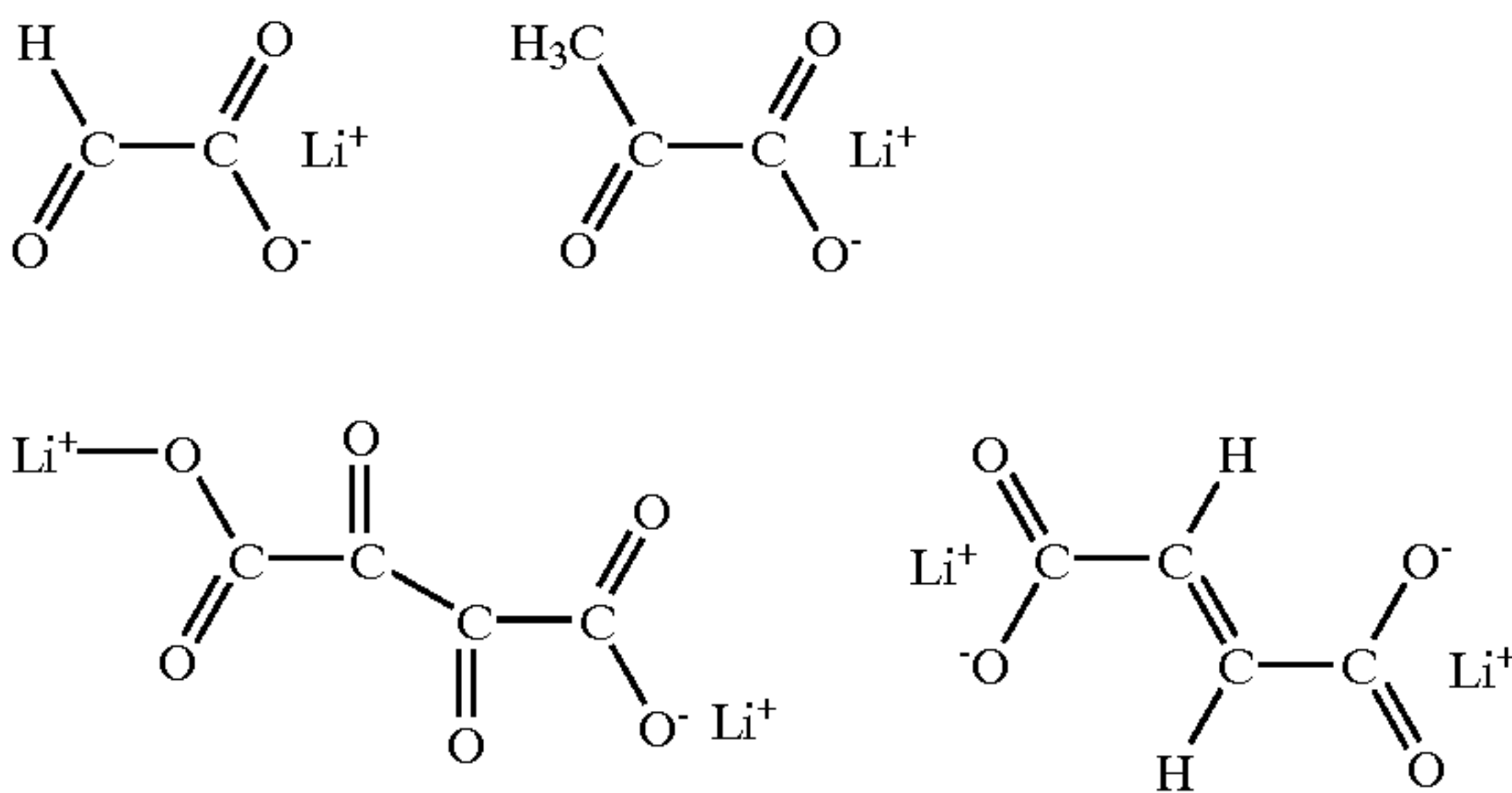
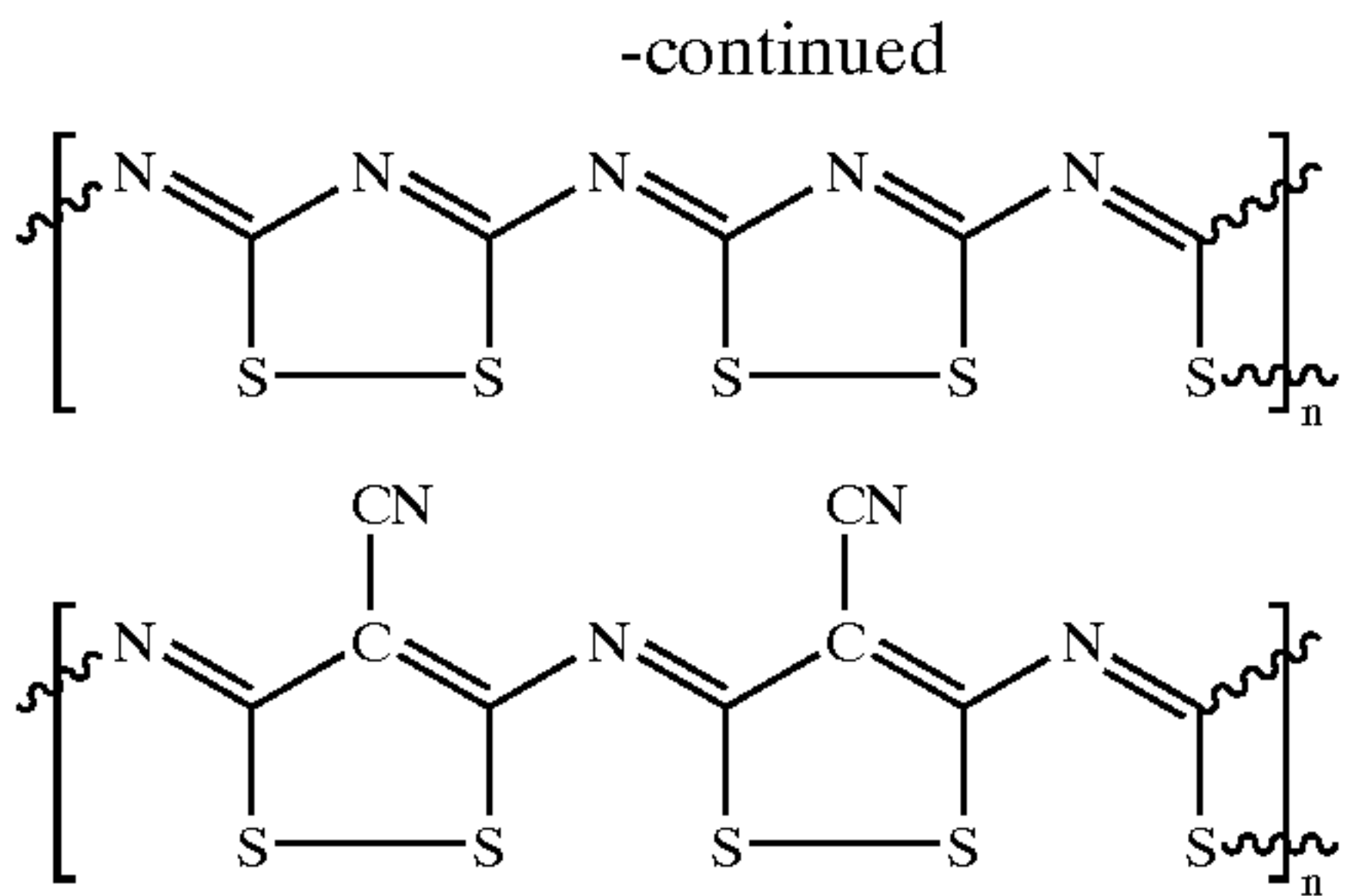
[0030] Another interesting aspect of certain compounds of the invention is their possibility to give, after oxidation beyond the normal reversible operating potential, an irreversible reaction liberating lithium ions and gaseous compounds such as carbon monoxide or carbon dioxide, nitrogen, ethylene or acetylene and their polymers. These products are eliminated from the generator medium (gas) or are inactive (polymers), and provide exceeding capacity that is useful to compensate for the loss of capacity equilibrium between the anode and the cathode, caused mainly by the appearance of a passivation layer during the first operating cycles of the generator.

[0031] The following anions are illustrate compounds of the present invention, and should not be considered as limiting its scope.

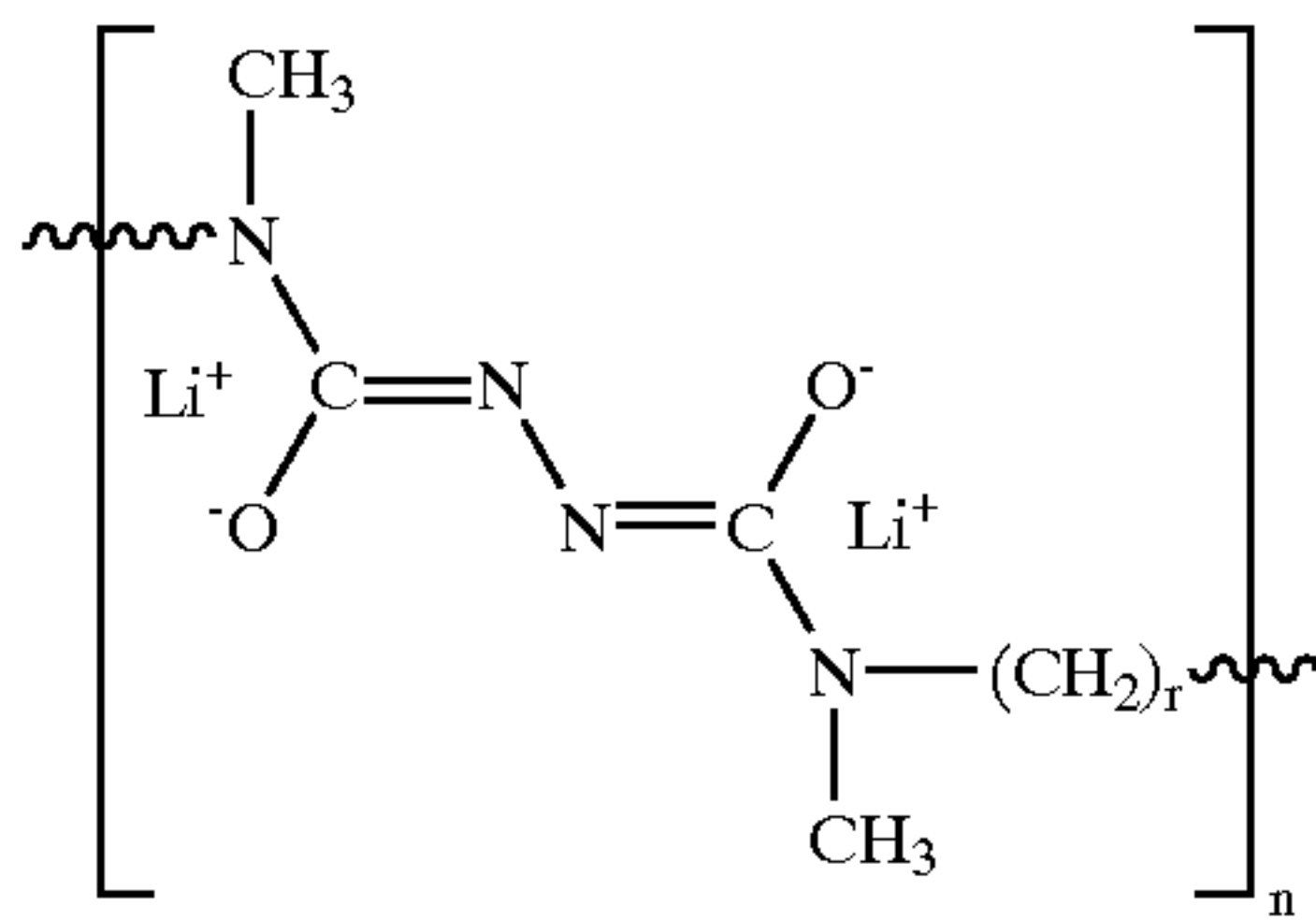


-continued

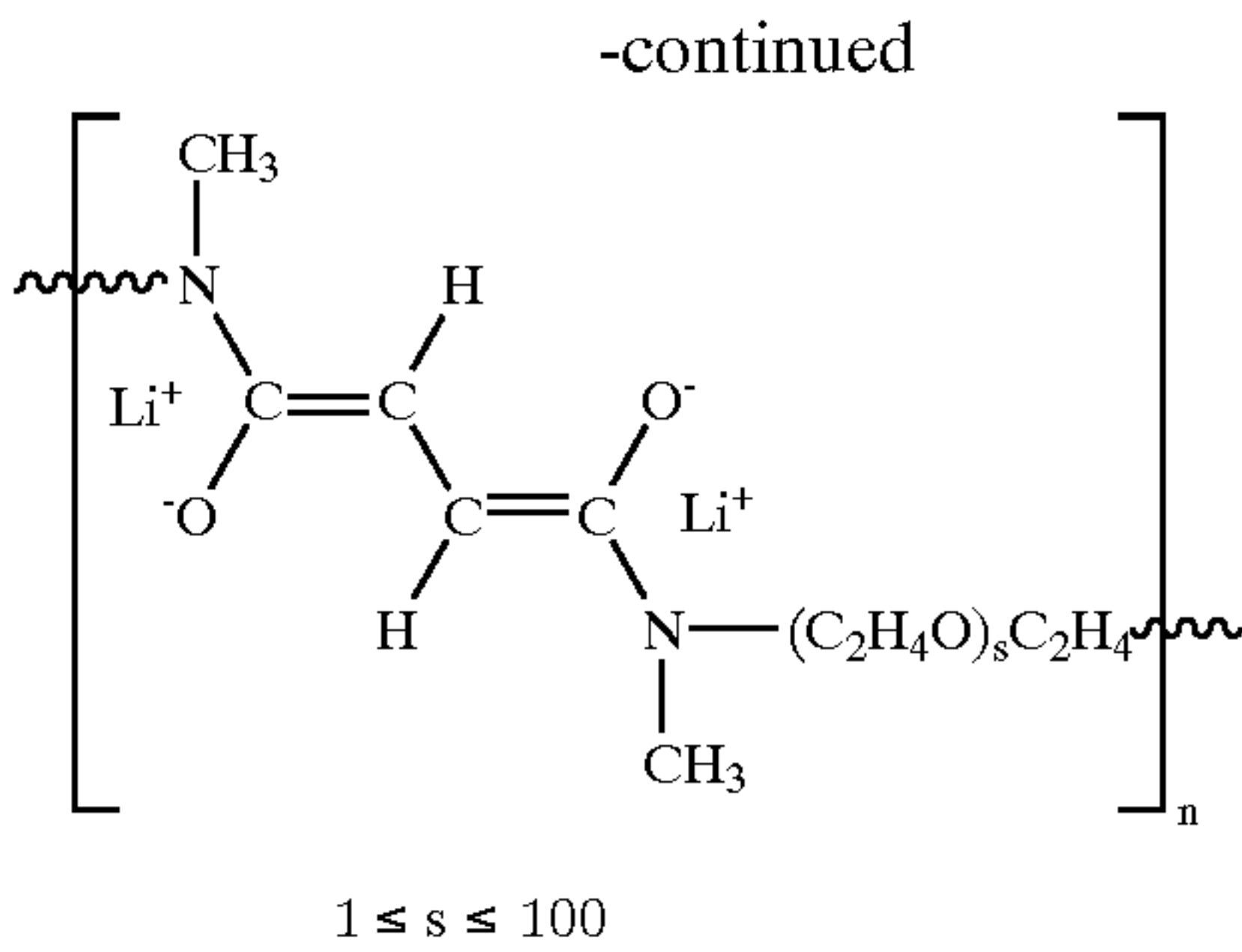




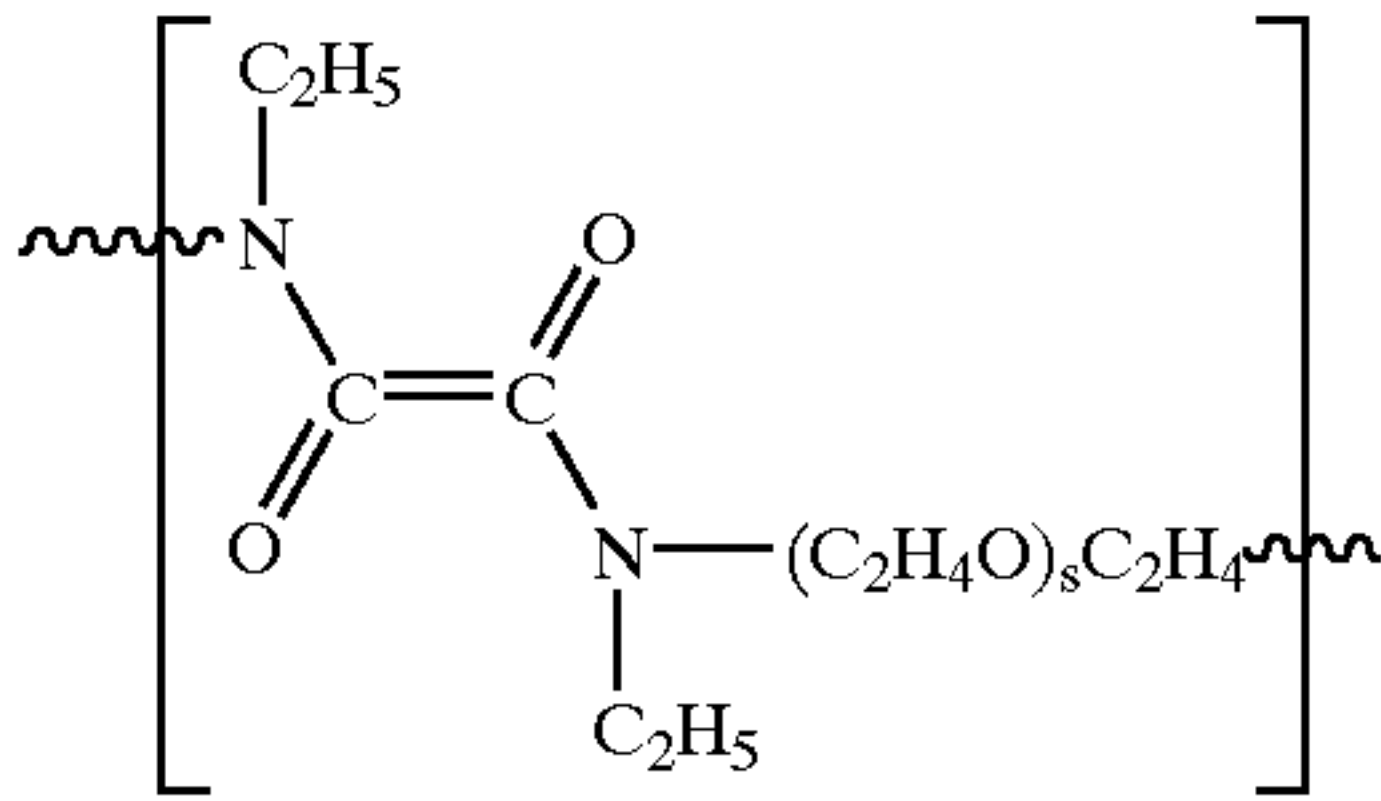
$2 \leq r \leq 12$



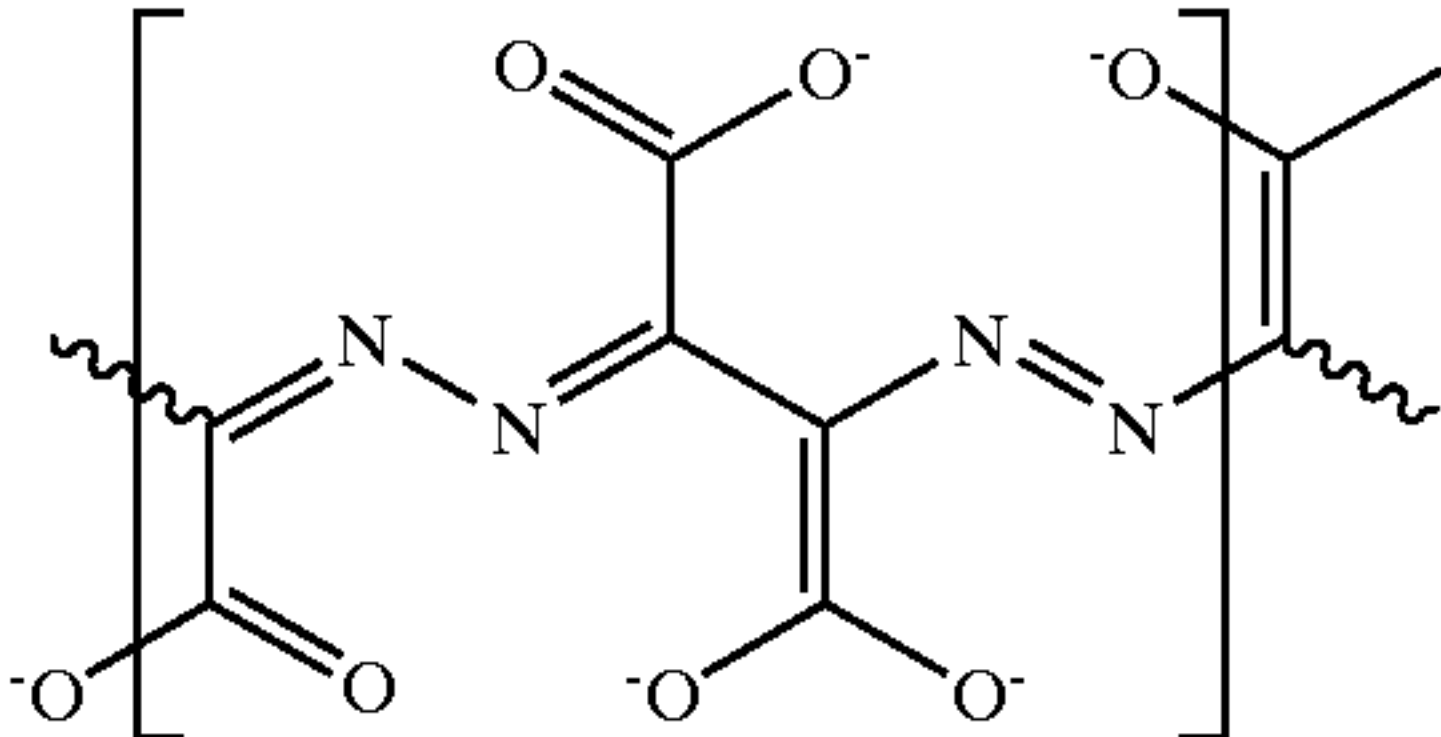
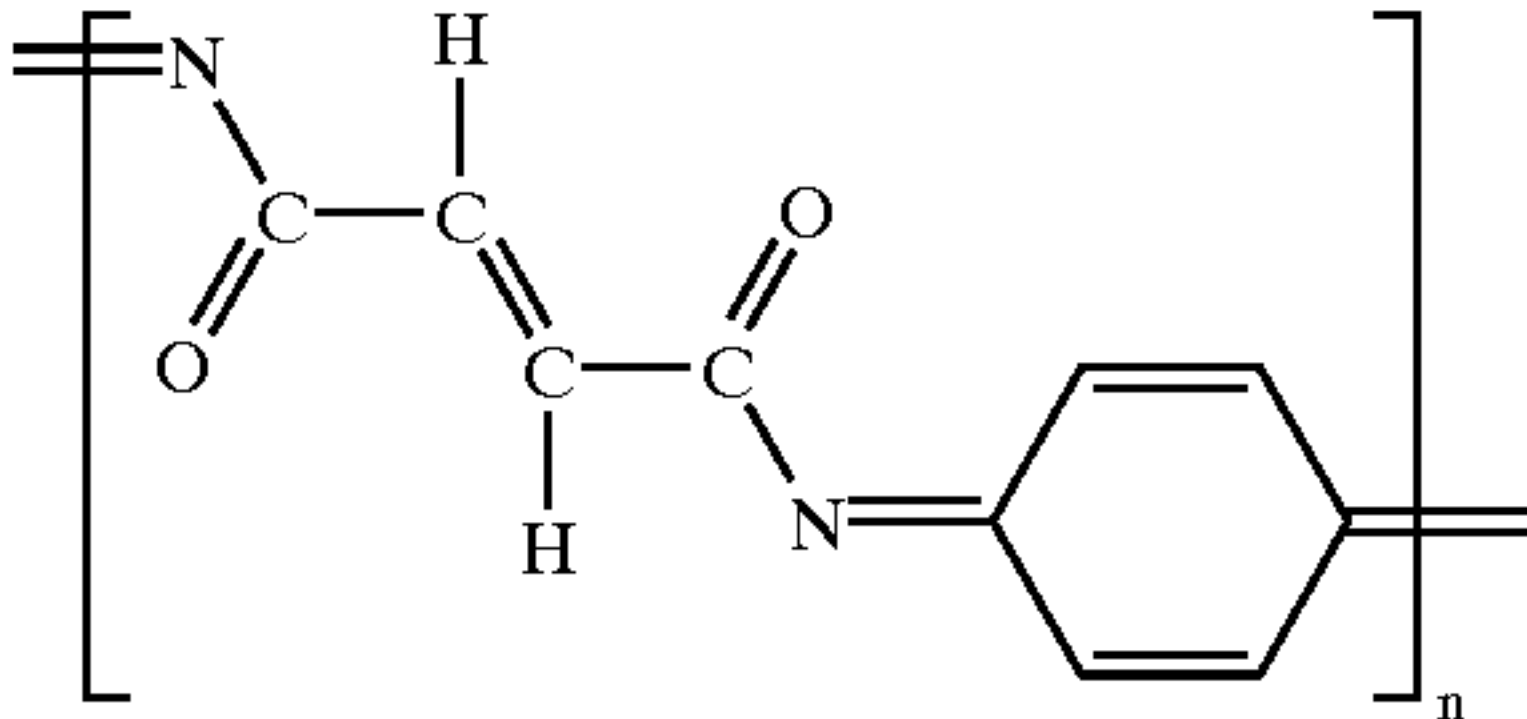
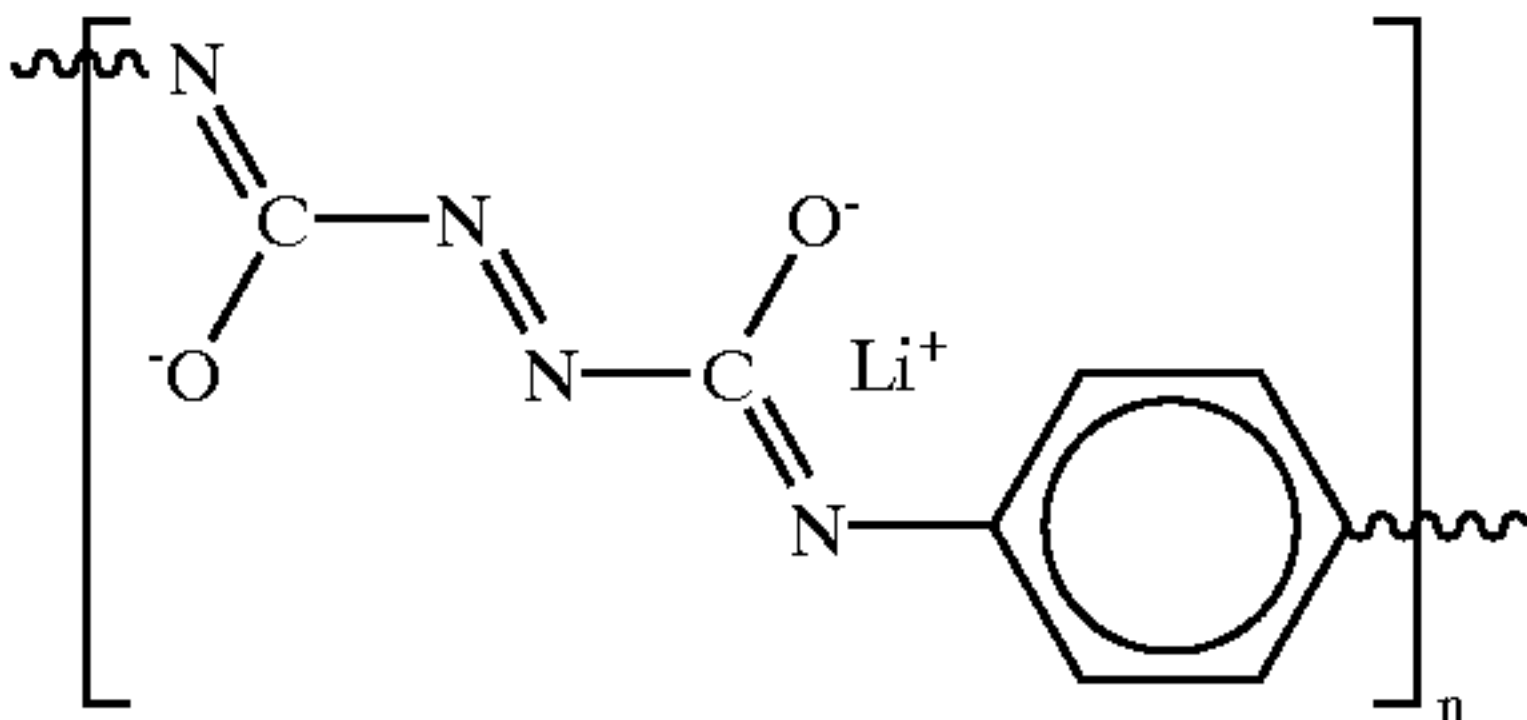
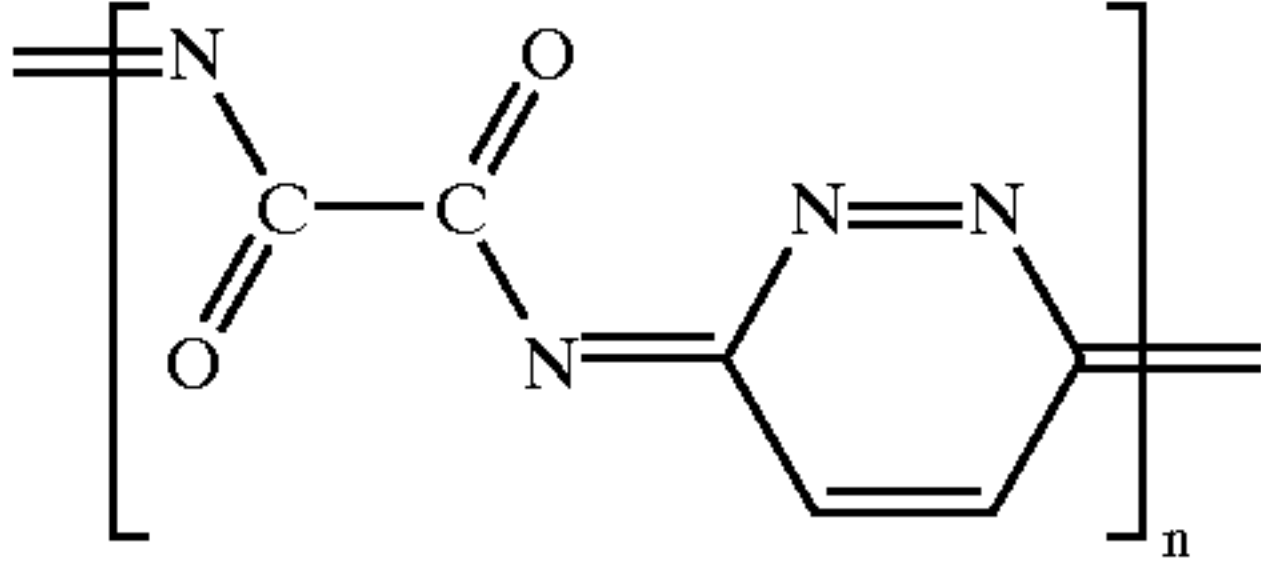
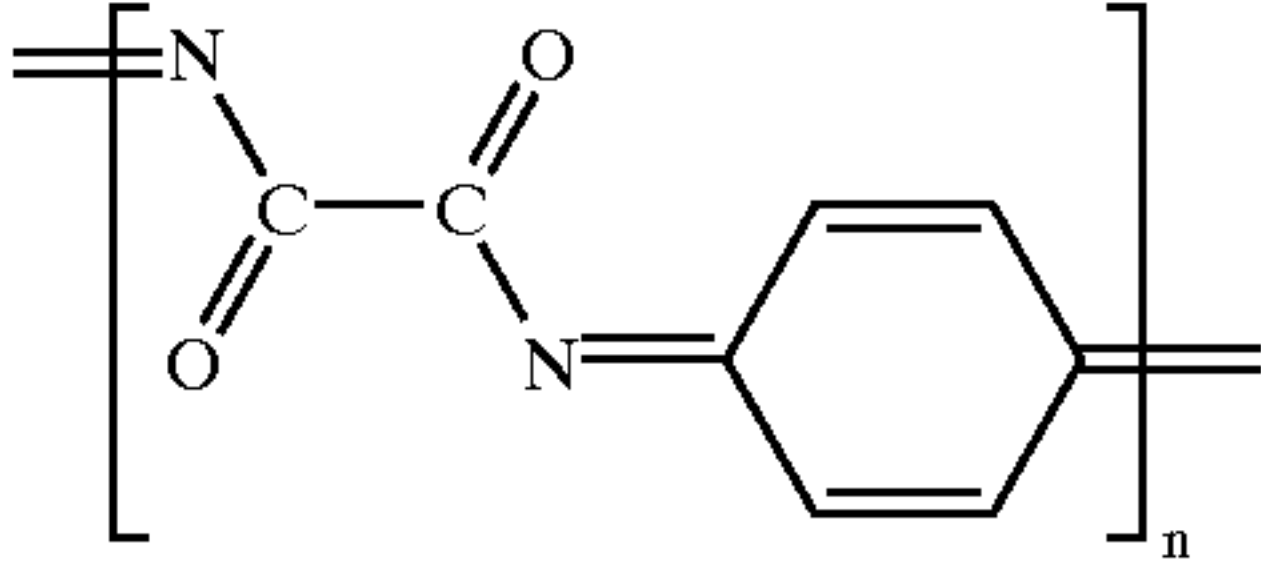
$2 \leq n \leq 10^4$



$1 \leq s \leq 100$



$1 \leq s \leq 100$

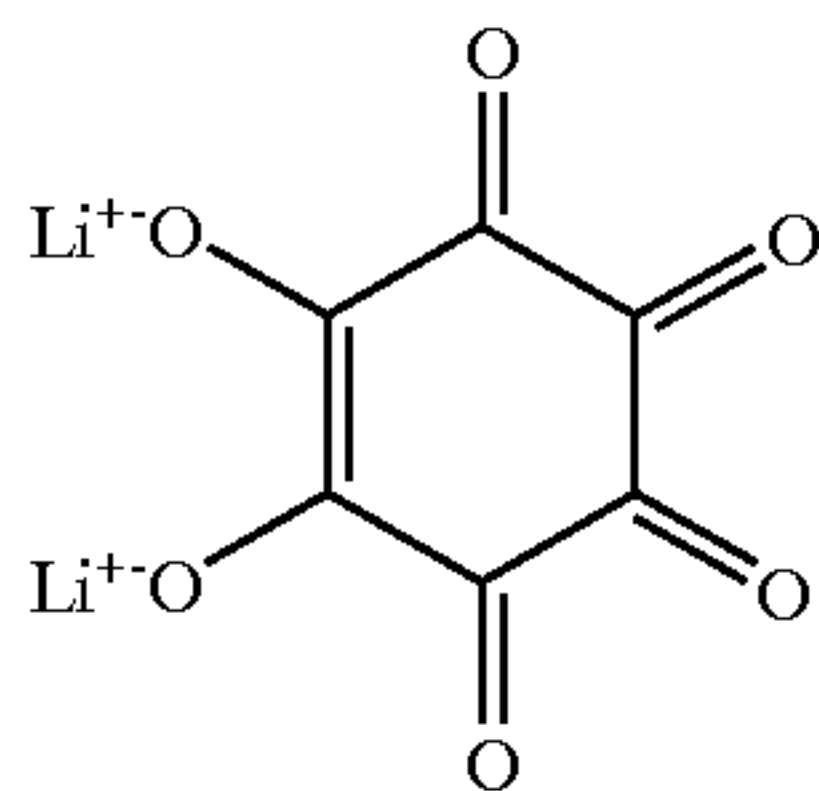


$4 \leq n \leq 10^4$

[0032] The following examples are provided to illustrate preferred embodiments of the present invention, and should not be considered as limiting its scope.

EXAMPLE 1

[0033] 2.10 g of dihydrated rhodizonic acid (Lancaster Windham) are treated with 839 mg of monohydrate lithium hydroxide in isopropanol. The suspension is filtered and the black precipitate is dried under primary vacuum at 50° C., to give the following lithium rhodizonate:



EXAMPLE 2

[0034] A lithium battery is fabricated with a film of lithium of a thickness of 30 nm, a polymer electrolyte made of a complex of ethylene polyoxide of a mass of 9×10^4 and lithium bis-trifluoromethanesulfonylamide (LiTFSI) to obtain a ratio of the number of oxygens of the polymer on the lithium ions of 12:1. The solution in a common solvent is spread, evaporated and dried to form a film of a thickness of about 80 μm . The positive electrode comprises a mixture of 40% v/v of lithium rhodizonate as prepared in example 1, 5% by weight of carbon black (Ketjen black®) and 5% v/v of the electrolyte of the electrolytic composition previously described, but obtained with a polymer of a molecular weight of 10^5 . Acetonitrile is added to the mixture, and the suspension obtained is homogenized by agitation with zircon balls in a stainless steel recipient for 24 h. The electrode is obtained by spreading the suspension on a stainless steel disk of 1.6 cm diameter to form after evaporation of the solvent, a layer of a thickness of 60 nm. The battery assembled in a neutral atmosphere (helium <1 ppm O_2 , H_2O) in the form of a battery-button by pressing the three components: anode-electrolyte-cathode and is tested at 80° C. in slow voltammetry with a digital potentiostat Macpile®. Two domains of activity corresponding each to a capacity of 305 mAh.g^{-1} are apparent at about 2.8 V and about 1.8 V with respect to the couple Li^+/Li^0 . For comparison purposes, the capacity of a manganese spinel based electrode LiMn_2O_4 possesses a theoretical maximum capacity of 153 mAh.g^{-1} at 2.9 V and modifications of this compound, in order to limit the dissolution of the manganese, such as the composition $\text{Li}_{1.05}\text{Mn}_{1.85}\text{Al}_{0.1}\text{O}_4$, have a capacity of 115 mAh.g^{-1} .

EXAMPLE 3

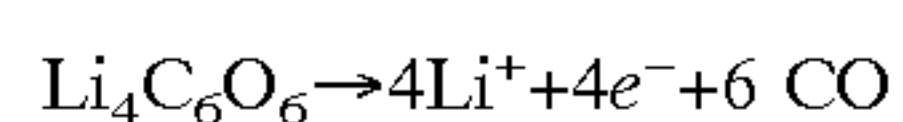
[0035] Tetrahydroxybenzoquinone is treated with an excess of lithium isopropoxide in solution in isopropanol to give the lithium tetra-salt corresponding to the following reaction:



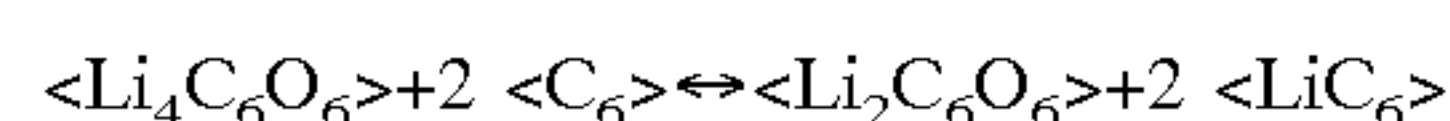
[0036] The black precipitate is filtered, dried and protected from exposure to air.

[0037] A "rocking chair" or "lithium ion-type" battery is fabricated by providing a graphite negative electrode (85% v/v) bonded with a copolymer of vinylidene fluoride and hexafluoropropene (PVDF), deposited on a thin sheet of

copper (8 mm) and corresponding to a capacity of 3.1 mAh.cm^{-2} for the composition LiC_6 . The positive electrode is a mixture of carbon black of the Ketjen black type (7% v/v), lithium tetra-salt of tetrahydroxybenzoquinone (73% v/v) and PVDF (10%) deposited on an aluminum collector of 10 mm. The capacity of the positive electrode for a reversible exchange of two electrons per molecule is 3.5 mAh.cm^{-2} . The electrolyte is made of a 1M solution of LiPF_6 in a mixture of ethylene carbonate of 2-tertobutoxyethyl-2'-methoxyethylether (50/50 v/v). The liquid is immobilized in a porous membrane (Celgard®) of a thickness of 25 mm. The battery is charged in an intermittent mode at 0.45 mAcm^{-2} for 8 hours and the potential stabilizes at 3.6 V. The capacity extracted during discharge at C/5, i.e. 5 hours to extract the nominal capacity, is of 3.8 mAh.cm^{-2} , and stable during cycling for over 100 cycles. The irreversible capacity of the first insertion of lithium in the carbon, which is necessary to the formation of a passivation layer, is obtained by over-oxidation of the lithium salt according the equation:



[0038] The reversible operation of the battery takes place according to the equation:



[0039] A generator identical to that of example 3 is fabricated by mixing two active compounds in the positive electrode, that is to say 0.9 mg/cm^2 of the lithium tetra-salt of tetrahydroxybenzoquinone and 16 mg/cm^2 of cobalt and lithium oxide LiCoO_2 . The generator is charged at 4.2 V and its cycling capacity is 2.5 mAh.cm^{-2} , which corresponds to 96% of the capacity of the cobalt oxide alone.

EXAMPLE 4

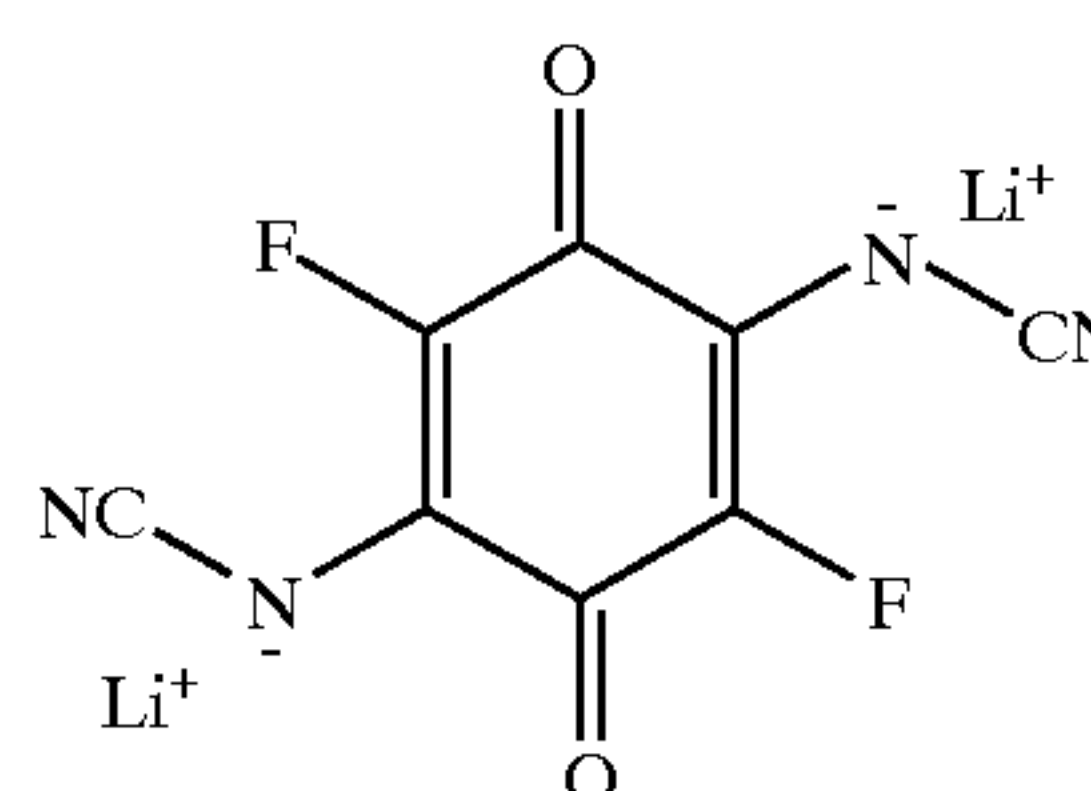
[0040] Potassium rhodizonate $\text{K}_2\text{C}_6\text{O}_6$ (Fluka) is treated to make an electrochemical generator in the conditions similar to those of example 2. The capacity is 210 mAh.g^{-1} , which is 93% of the theoretical capacity, which is 225 mAh.g^{-1} .

EXAMPLE 5

[0041] Copper rhodizonate is prepared by reacting 3.5 g of dihydrated rhodizonic acid with 3.5 g of dihydrated copper acetate in methanol. After evaporation of the solvent and the acetic acid produced by the reaction, copper rhodizonate is dried at 110° C. under primary vacuum. The capacity obtained in a generator comprising a lithium anode and a gel-type electrolyte (45% copolymer of vinylidene fluoride and hexafluoropropene, 55% solution 1 M of LiBF_4 in γ -butyrolactone) is of 450 mAh.g^{-1} and corresponds to 94% of the theoretical capacity for 4 electrons between 3.3 et 2.5 V vs. Li^+/Li^0 .

EXAMPLE 6

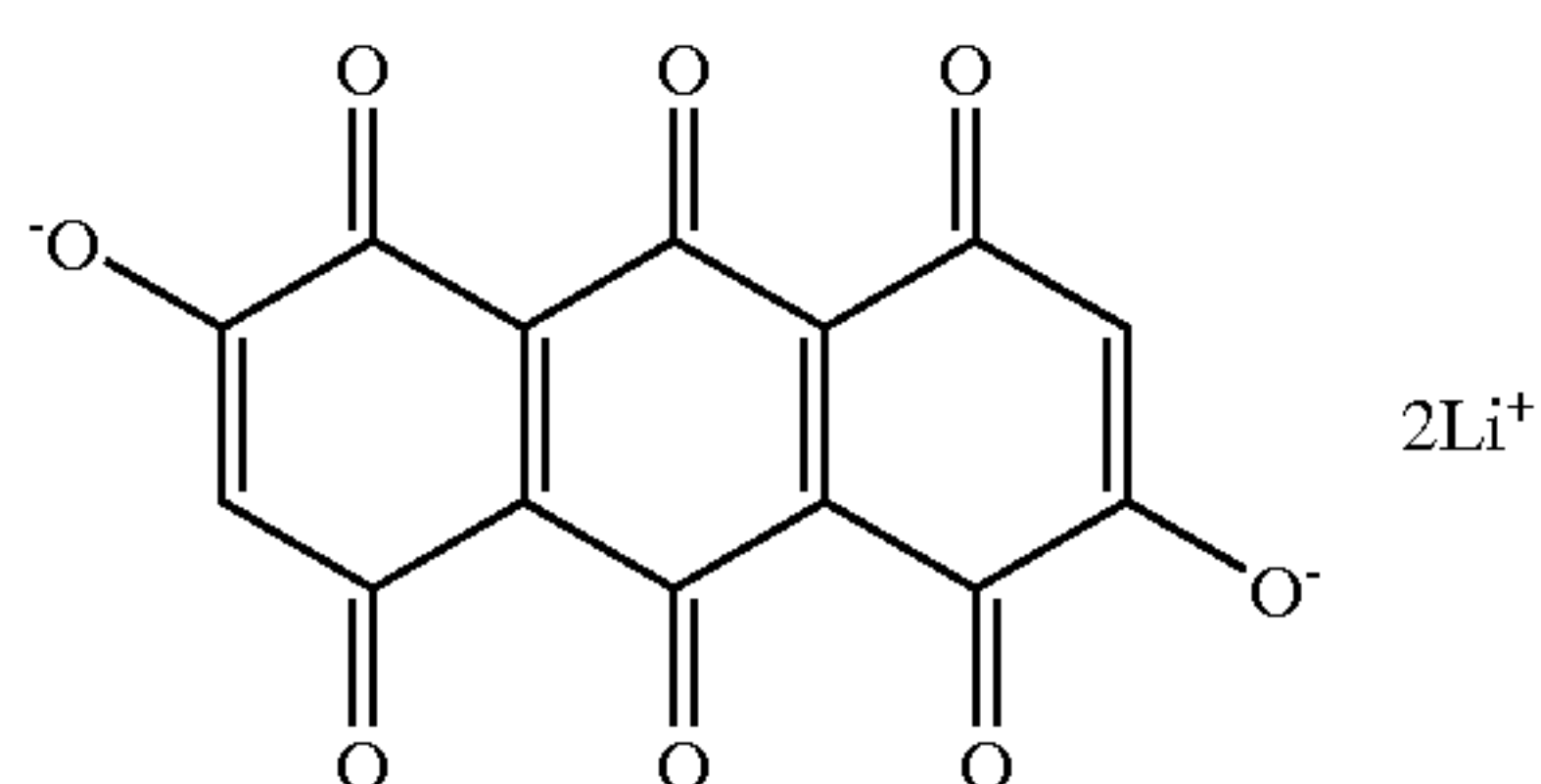
[0042] The compound



[0043] is obtained by reacting two equivalents of the lithium di-salt of the cyanamid Li_2NCN on tetrafluorobenzoquinone in DMF. The lithium fluoride is separated by centrifugation and the blue lithium salt corresponding to the above formula is precipitated in ether. This compound possesses a capacity of 235 mAh.g^{-1} at 2.6 V vs. $\text{Li}^+/\text{Li}^\circ$.

EXAMPLE 7

[0044] Rufigallic acid is prepared according to the method of Robiquet (*Ann.* 19, (1836), 204) by condensing gallic acid in concentrated sulfuric acid. The hexasubstituted lithium salt is prepared by suspending rufigallic acid in THF under a neutral atmosphere and treatment with lithium isopropoxide. The resulting salt is filtered and dried under dry nitrogen. Oxidation to the diquinonic form is performed by treating 4.0 g of this compound with a stoichiometric amount of [bis(trifluoroacetoxy)iodo]benzene (10.18 g) in acetonitrile. After filtration and drying, the following compound is obtained:



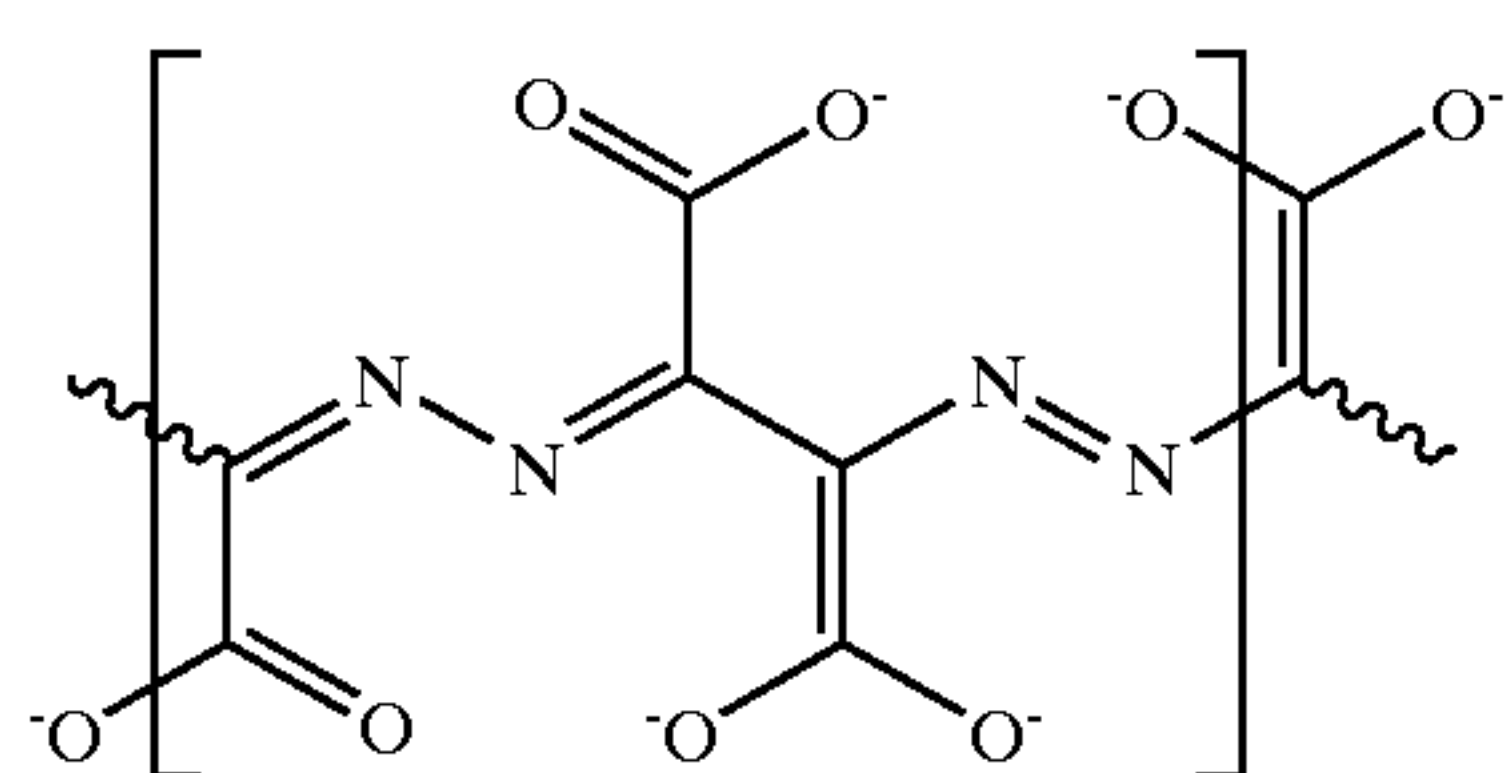
[0045] This compound has a reversible capacity of 358 mAh.cm^{-2} between 2.5 and 3.2 V vs. $\text{Li}^+/\text{Li}^\circ$.

EXAMPLE 8

[0046] 1.40 g of trans-trans muconic acid (Sigma) are treated with 0.739 g of lithium carbonate in methanol. After evaporation and vacuum drying, a generator similar to that of example 2 is fabricated by using a cathodic mixture of 25% v/v of lithium muconate, 10% of Ketjen black and 65% of polyelectrolyte. The compound has a reversible capacity of 0.8 electron per formula at 1.3 V with respect to lithium. This compound can be used as a negative electrode in lithium-ion type batteries.

EXAMPLE 9

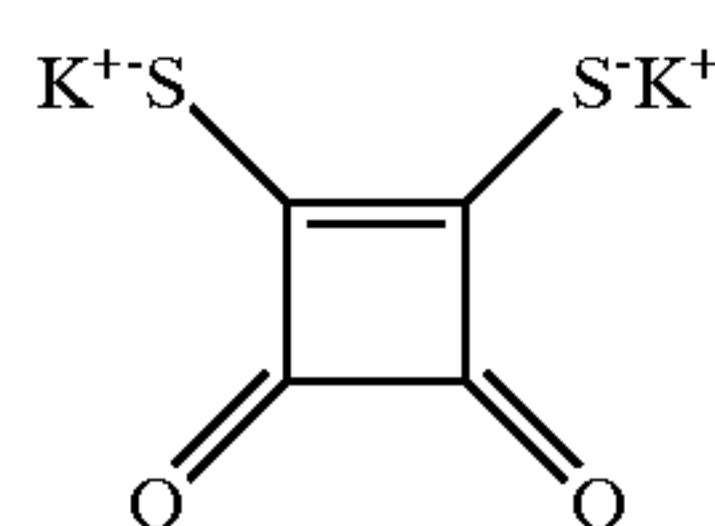
[0047] A polymer possessing conjugated azino functions (diazo in a reduced state) is prepared by action of 5 g of hydrazine monohydrate $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ on the sodium salt of dihydroxytartric acid (22.6 g, Janssen Chemicals) in acetic acid, under agitation for 24 hours. The dark brown polymer is precipitated in isopropanol, separated by filtration and dried. The compound possesses redox properties of 2 electrons per repetitive unit of the polymer, that is to say a capacity of 290 mAh.g^{-1} . The lithium salt obtained by passage through an ion exchange column has a capacity of 360 mAh.g^{-1} . The formula of the polymer reduced to 50% of its capacity is:



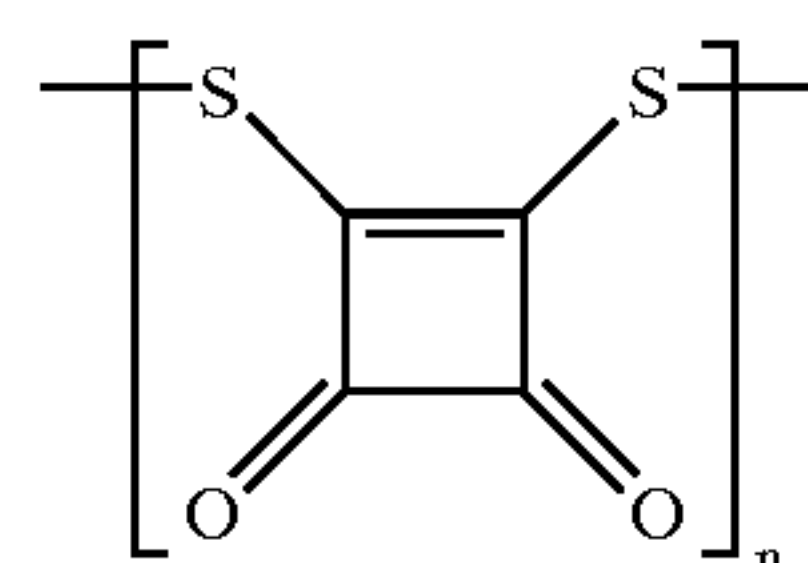
EXAMPLE 10

[0048] The potassium salt of dithiosquaric acid is prepared by reacting potassium hydrosulfide (14.43 g, Alpha) on

dibutoxy-3,4-cyclobutanel,2-dione (22.62 g Aldrich) in ethanol. A yellow salt is obtained and recrystallized in a mixture water-ethanol, and is of formula:



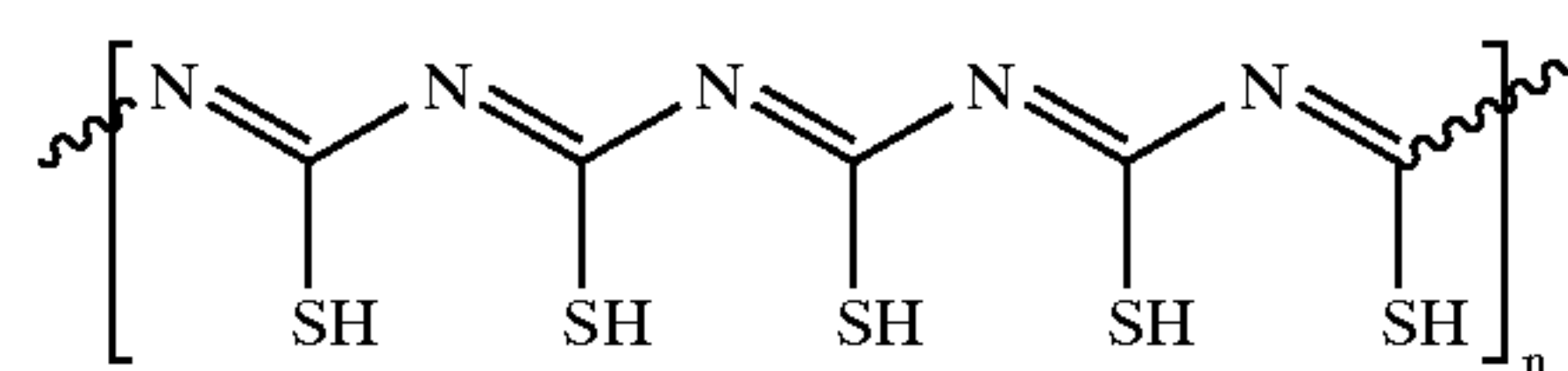
[0049] To 18 g of this salt in suspension in acetonitrile are added under mechanical agitation a solution of tetrabutylammonium tribromide (34.6 g) in acetonitrile. After one hour, the yellow precipitate is filtered and dried to give:



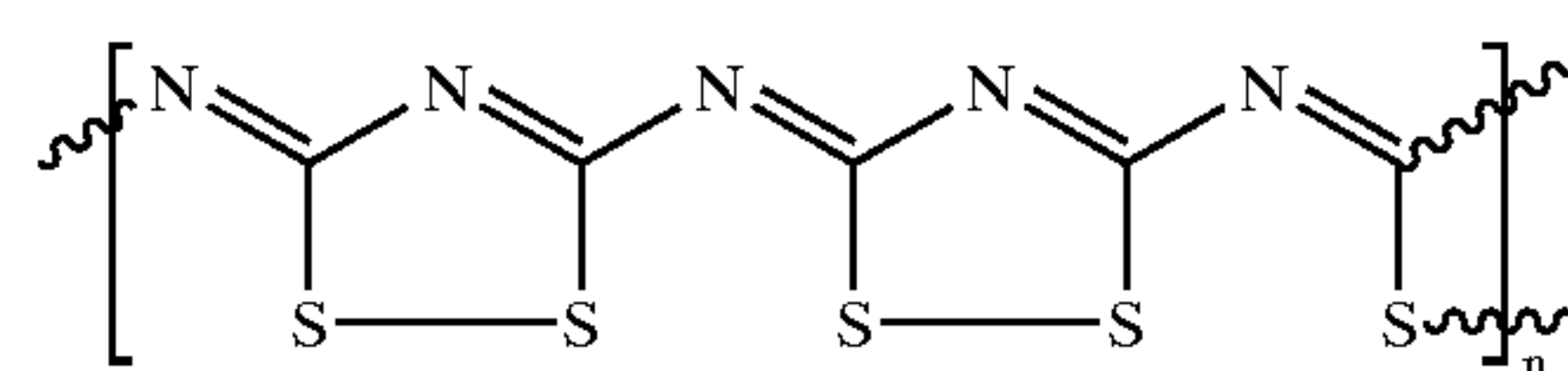
[0050] This compound possesses a reversible capacity of 385 mAh.g^{-1} at an average potential of 2.8 V vs. $\text{Li}^+/\text{Li}^\circ$ and its solubility in electrolytes like propylene carbonate and its mixtures or the polymers solvating based on ethylene polyoxide is negligible, contrary to polydimercapthiadiazole.

EXAMPLE 11

[0051] A Schiff polybase, poly(thiocyanic) acid, is prepared by reacting thiophosgene on thiourea in propylene carbonate in the presence of pyridine. The dark brown suspension is poured in 100 ml of water and the precipitate is filtered and washed with water. The product corresponds to the composition $[\text{C}(\text{SH})=\text{N}]_n$ with a developed formula:



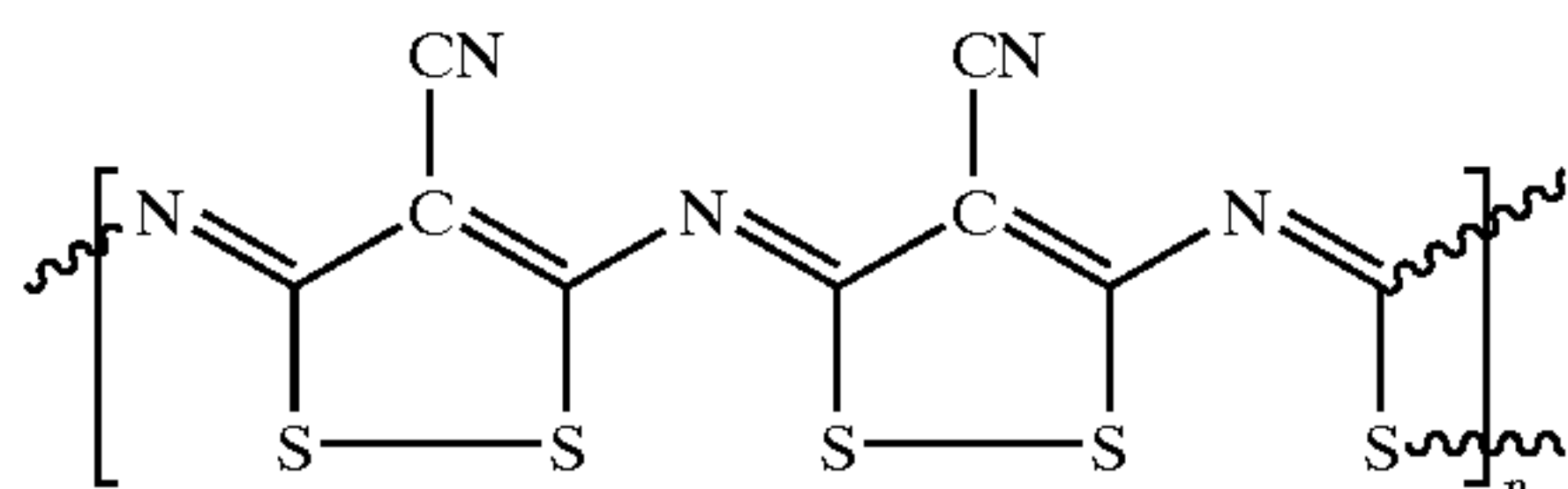
[0052] The polymer in its reduced form is oxidized by iodine in solution in acetonitrile in the presence of pyridine, and the suspension remaining is washed with acetonitrile until a colorless eluate is obtained. The brown-black powder corresponds to the oxidation of the thiol groups to give the polymer:



[0053] An electrochemical generator similar to that of example 2 using a positive electrode containing 40% v/v of the compound thus obtained shows a capacity of 360 mAh.g^{-1} between 3 and 2.4 V vs. $\text{Li}^+/\text{Li}^\circ$, that is to say 75% of the theoretical capacity which is 478 mAh.g^{-1} .

EXAMPLE 12

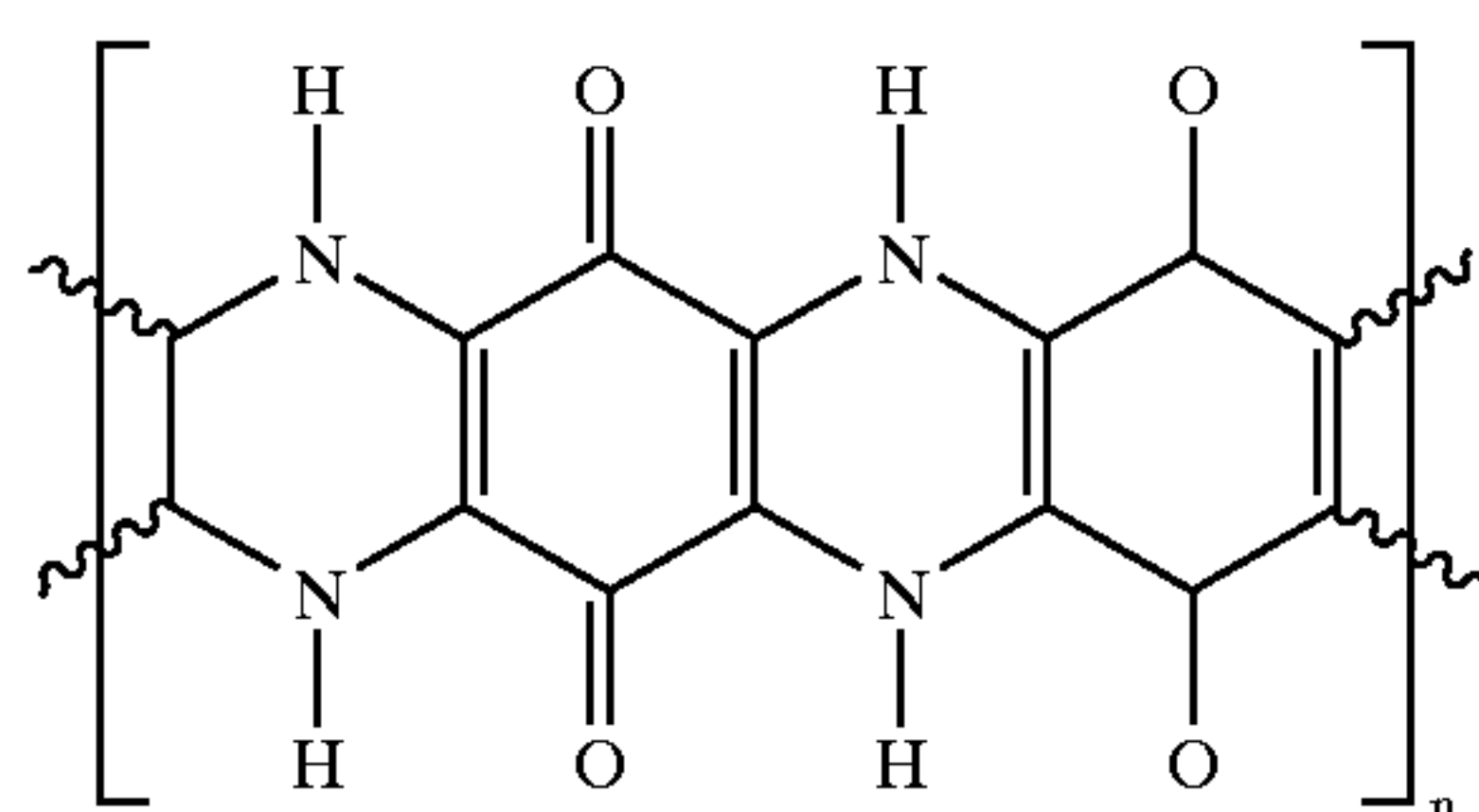
[0054] In the same manner as in example 11, the alternate copolymer of formula:



[0055] is prepared by replacing thiourea with the thioamide of cyanoacetic acid. The polymer obtained after oxidation is a black powder having a capacity of 555 mAh.g^{-1} , with 50% between 3.2 V and 2.4 V vs. $\text{Li}^+/\text{Li}^\circ$.

EXAMPLE 13

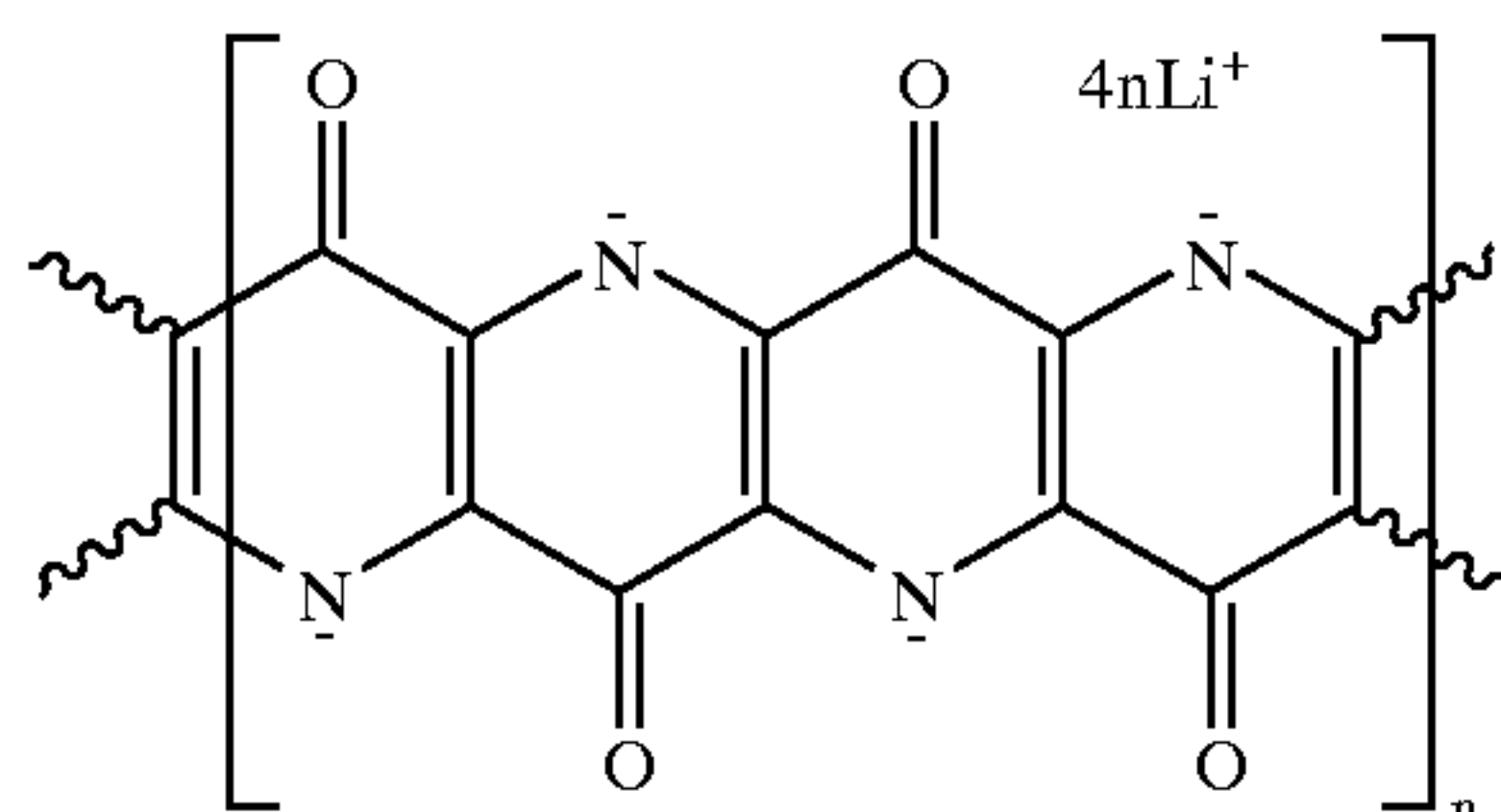
[0056] Tetraaminobenzoquinone is prepared according to the method of Wallenfel & al. (*Ann.* 1963, 667). 16.8 g of this compound and 2.46 g of chloranil (tetrachlorobenzoquinone) are mixed in a ball mill, and heated under argon at 250°C . in a Büchi TO51 oven followed by a treatment at 350°C . under vacuum. The compound obtained corresponds to the polyquinone-azine of formula:



[0057] The lithium salt of this compound is obtained by treating a suspension of the polymer with a solution of lithium isopropoxide in isopropanol. This compound has a reversible capacity of 345 Ah.g^{-1} between 2.4 and 3 V vs. $\text{Li}^+/\text{Li}^\circ$, that is to say 75% of the theoretical capacity which is 420 mAh.g^{-1} . The lithium salt of this polymer can also be obtained directly by reaction of tetrachlorobenzoquinone on lithium nitride in the molar ratio 1:2 by cogrinding in anhydrous DMF.

EXAMPLE 4

[0058] A polymer perfectly alternated between ethylene and carbon monoxide is obtained according to the method of Hiraguri et al. (*J. Am. Chem. Soc.*, 1987, 109, 3779). 56.06 g of this polymer are dissolved in hexafluoropropanol and treated with 10.39 g of lithium nitrite under reflux. The conjugated polymer appears under the form a black precipitate which is the lithium salt of formula:



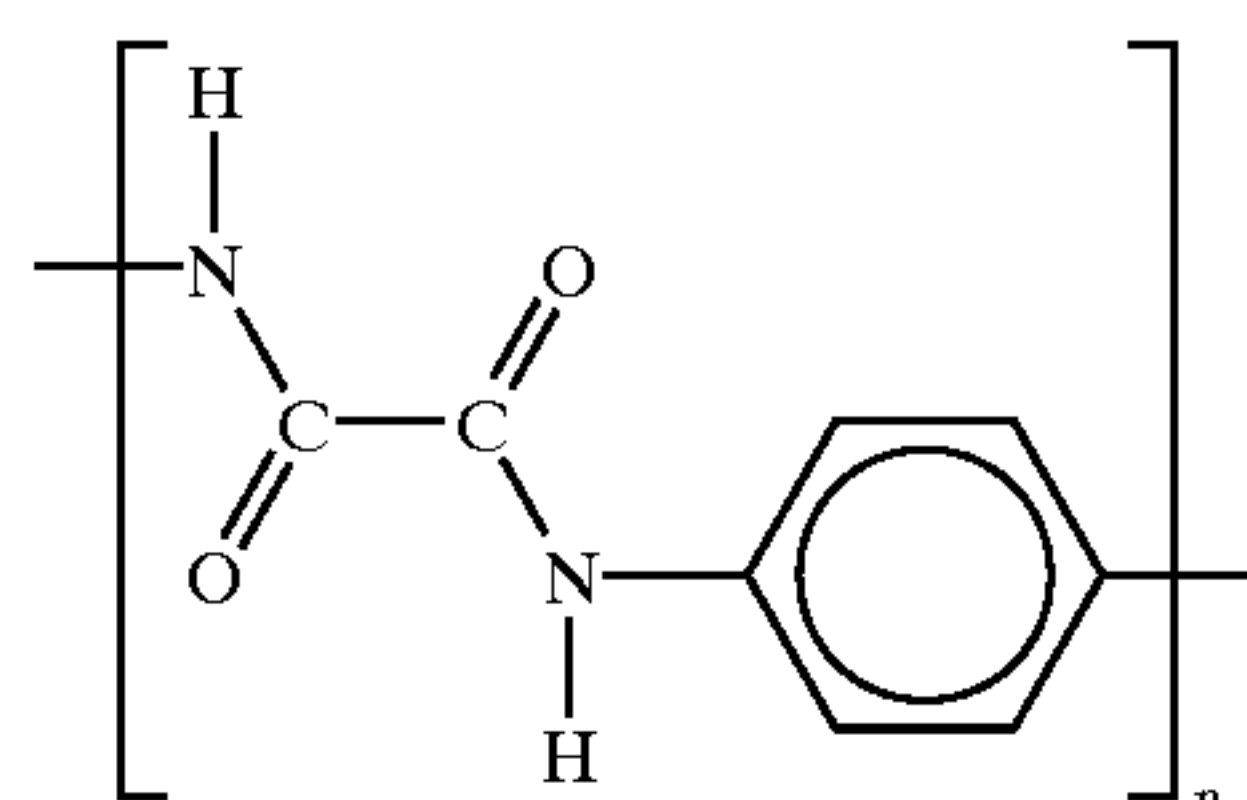
EXAMPLE 15

[0059] Azino(bisacetique) acid is prepared by reacting hydrazine hydrate in a stoichiometric amount with glyoxylic

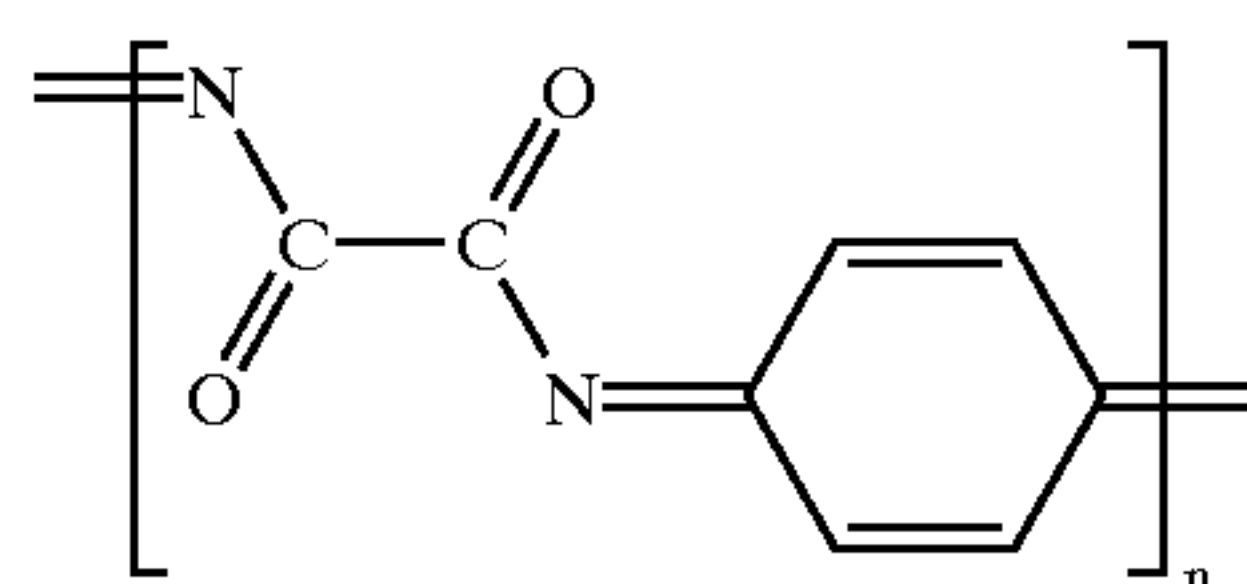
acid (Sigma) in isopropanol. The yellow-orange precipitate is dried and filtered, and the lithium salt is prepared in a solution methanol-water (50:50) by adding a stoichiometric amount of lithium carbonate. The salt is dried under vacuum and tested in conditions similar to those of example 7. This compound has a reversible redox activity at 1.7 V with respect to lithium.

EXAMPLE 16

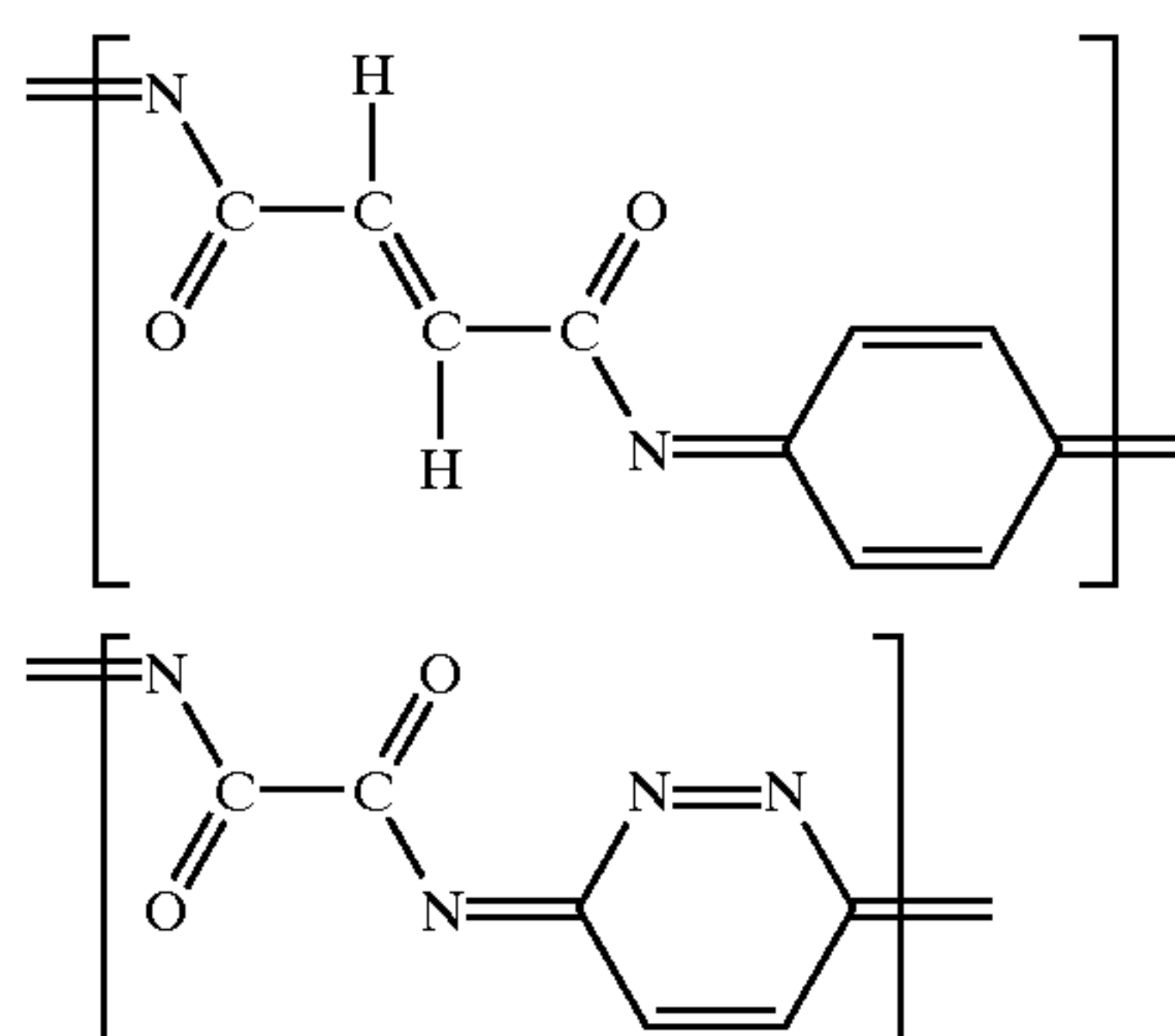
[0060] A polymer of the polyamide type of formula:



[0061] is obtained by polycondensation of methyl oxalate with 1,4-phenylene diamine in DMF. The reduced polymer is transformed in the oxidized quinoneimine form by reaction with bis[(trifluoroacetoxy)iodo]benzene in dichloromethane. The product has the developed formula:



[0062] It has a redox couple at 2.7 V vs. $\text{Li}^+/\text{Li}^\circ$ for a capacity of 310 mAh.g^{-1} (theoretical 347). Similar polymers are prepared by reaction of trifluoroethyl fumarate on 1,4-phenylene diamine (2.7 V vs. $\text{Li}^+/\text{Li}^\circ$) or oxalyl chloride on 3,6-diamino pyridazine (2.9 V vs. $\text{Li}^+/\text{Li}^\circ$).



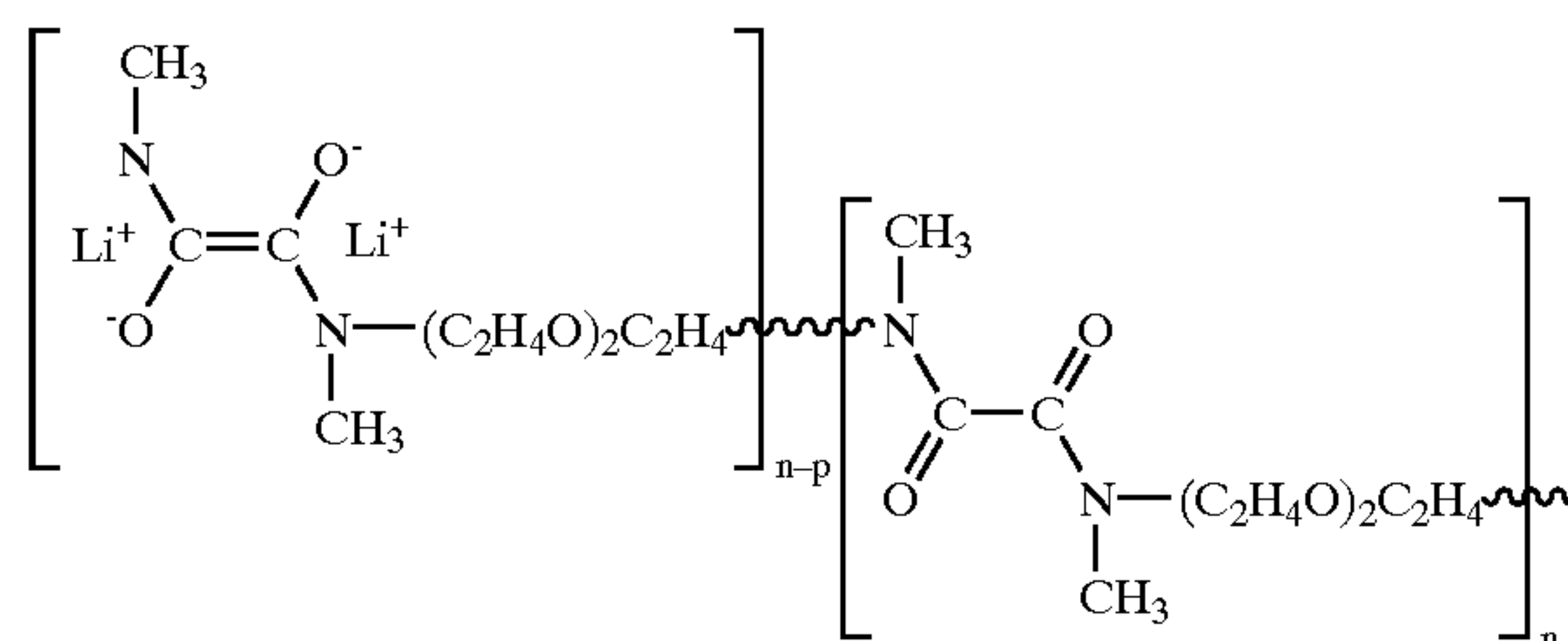
EXAMPLE 17

[0063] A redox polymer is prepared by condensing fumaryl chloride on N,N'-dimethylhexamethylenediamine in solution in DMF, in the presence of two equivalents of pyridine. The polymer is precipitated in water and purified by dissolution in acetone and reprecipitation in methanol.

This polymer, mixed with carbon black, shows a redox activity at 1 V vs. $\text{Li}^+/\text{Li}^\circ$ for a capacity of 195 mAh.g^{-1} (theoretical 247).

EXAMPLE 18

[0064] In the same manner as in Example 10, a redox polymer possessing an ionic conductivity and produced by the polycondensation of oxalyl-diimidazole on 1,8-bis(methylamino)-3,6-dioxaoctane (Janssen) in DMF is prepared. This polymer also shows a redox activity at 1 V vs. $\text{Li}^+/\text{Li}^\circ$. At the neutral state, the polymer possesses complexing properties towards salts and an ionic conductivity facilitating the redox reaction. The structure of this polymer in a partially reduced state is

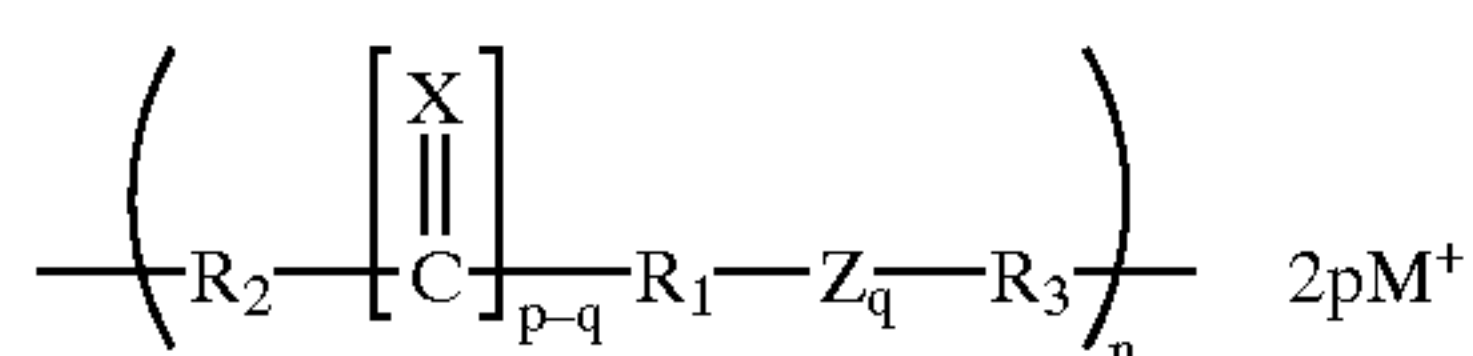


[0065] An amorphous copolymer can be obtained by using a mixture of the preceding amine with 1,5-bis(methylamino)-3-oxapentane. In the same manner, the oxalyl groups can be substituted with fumaryl or muconyl groups.

[0066] While the invention has been described in connection with specific embodiments thereof, it will be understood that it is capable of further modifications, and this application is intended to cover any variations, uses or adaptations of the invention following, in general, the principles of the invention, and including such departures from the present description as come within known or customary practice within the art to which the invention pertains, and as may be applied to the essential features hereinbefore set forth, and as follows in the scope of the appended claims.

What is claimed is:

1. A redox compound having at least one state of oxidation state represented by the general formula:



wherein

M^+ represents an alkaline metallic cation, an alkaline-earth cation, a transition metal cation, a rare earth cation, an organometallic cation, an organic cation of the "nium" type, a repetitive unit of a cationic oxidized conjugated polymer, or a monomeric or polymeric cation optionally having a redox character;

X is oxygen, NCN, or $\text{C}(\text{CN})_2$;

Z is $\text{C}-\text{Y}$ or N;

Y represents oxygen, sulfur, NCN, $-\text{C}(\text{CN})_2$, with the proviso that when Y is sulfur and n is ≤ 4 , then X is oxygen;

R_1 is absent, O, S, NH, $-(\text{C}=\text{C})_r-$, $-(\text{W}=\text{W})_r-$ wherein W is independently CR^6 or N; r varies between 1 and 12; and R^6 is H, halogen, CN, or C_{1-12} alkyl, C_{2-12} alkenyl or C_{6-14} aryl optionally having one or more substituents oxa, aza or thia; and wherein 2 R^6 groups can be bonded to form a cycle comprising from 3 to 7 members;

R^2 and R^3 are the same or different and are absent, a carbonated divalent radical, optionally substituted with aza, oxa or thia;

q varies between 0 et p;

p varies between 1 and 5;

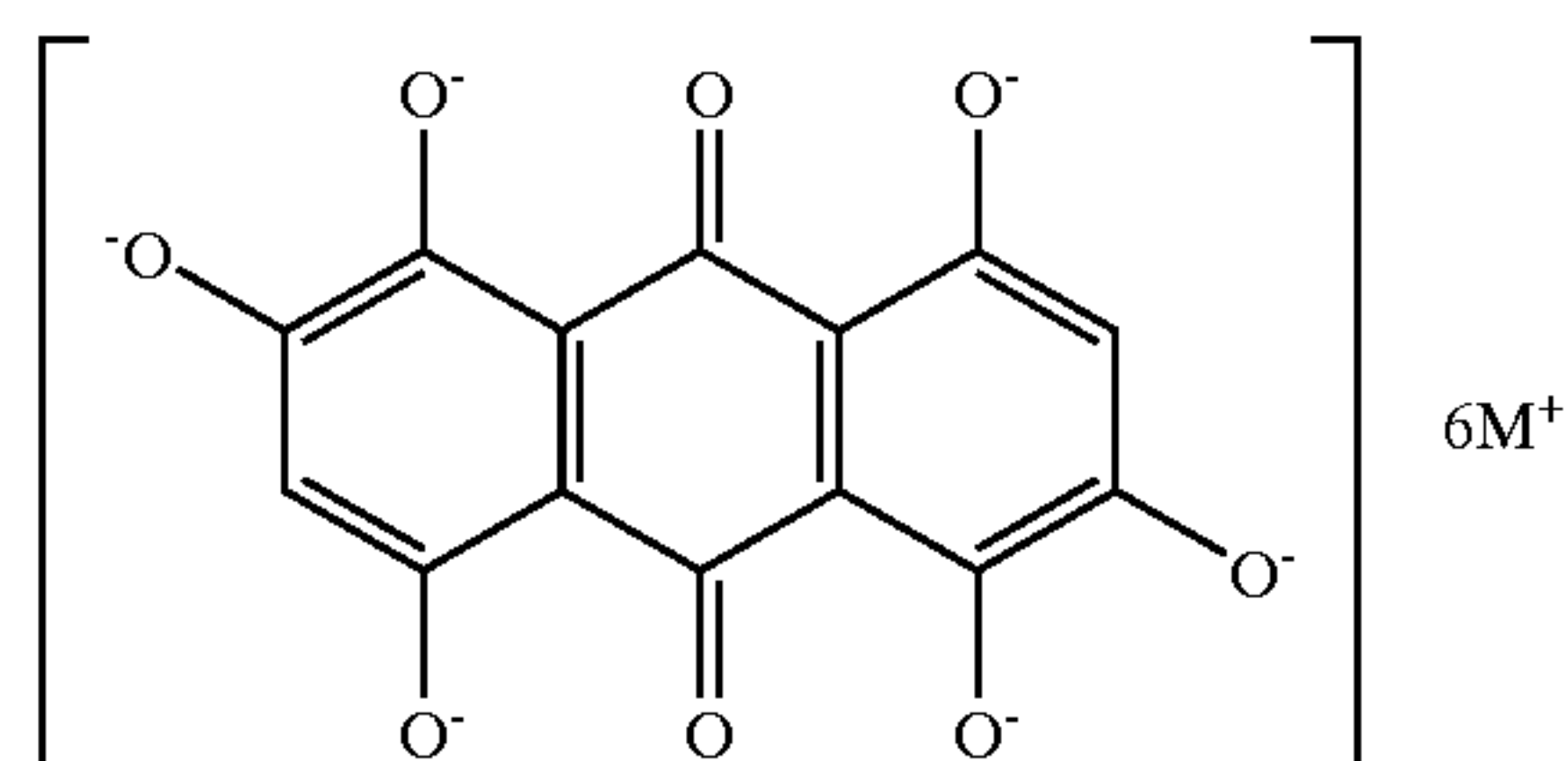
n varies between 1 and 10^4 ; and

wherein two of R^1 , R^2 and R^3 can be bonded together to form a cycle comprising 3 to 7 members.

2. A compound according to claim 1 characterised in that it is:

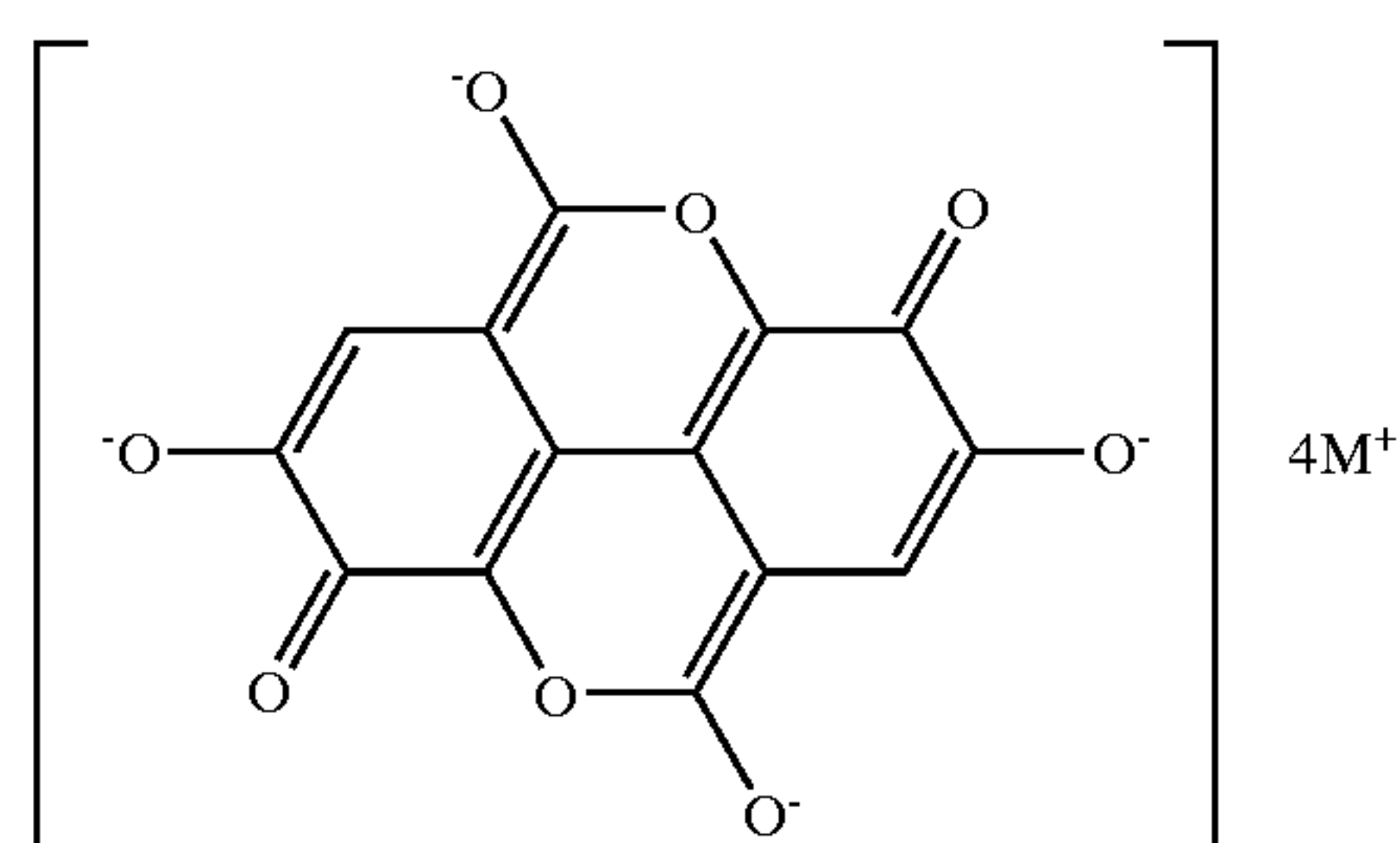
a rhodizonic acid salt;

a rufigallic acid salt represented by the formula



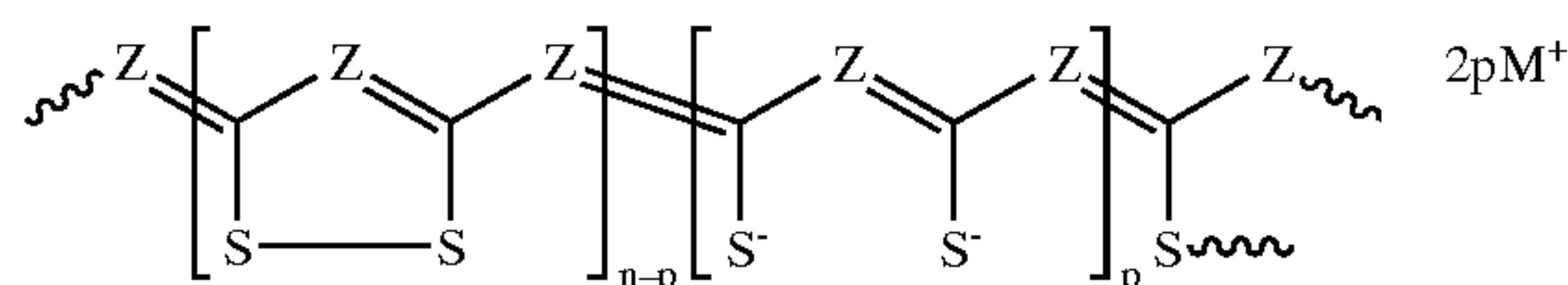
and its oxidation compounds;

an elagic acid salt represented by the formula



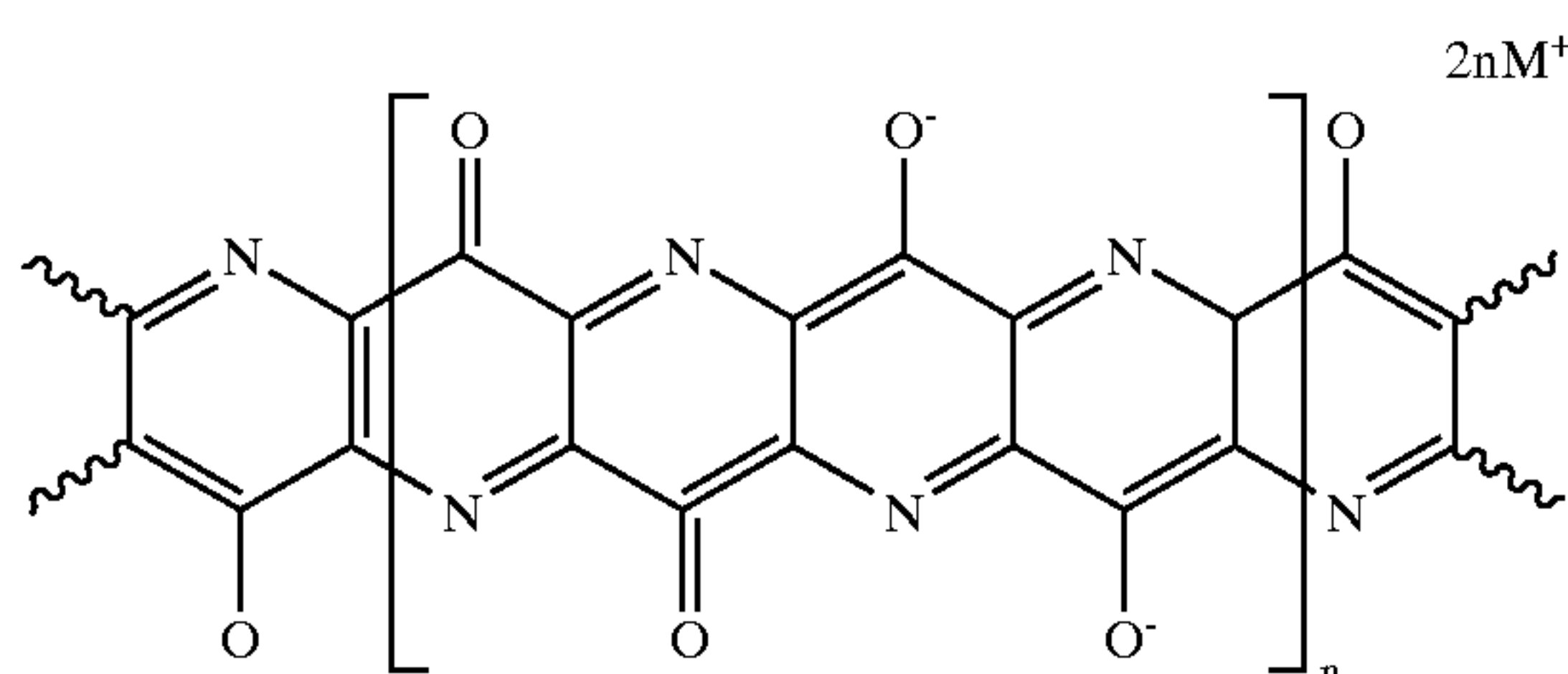
and its oxidation compounds, wherein the oxygen atoms with a double bond can be replaced with a group NCN or $\text{C}(\text{CN})_2$;

a polymer of thiocyanic acid or 1-cyano-2-mercaptoacetylene represented by the formula



and its oxidation and reduction products, wherein $Z=N$ or $C-CN$;

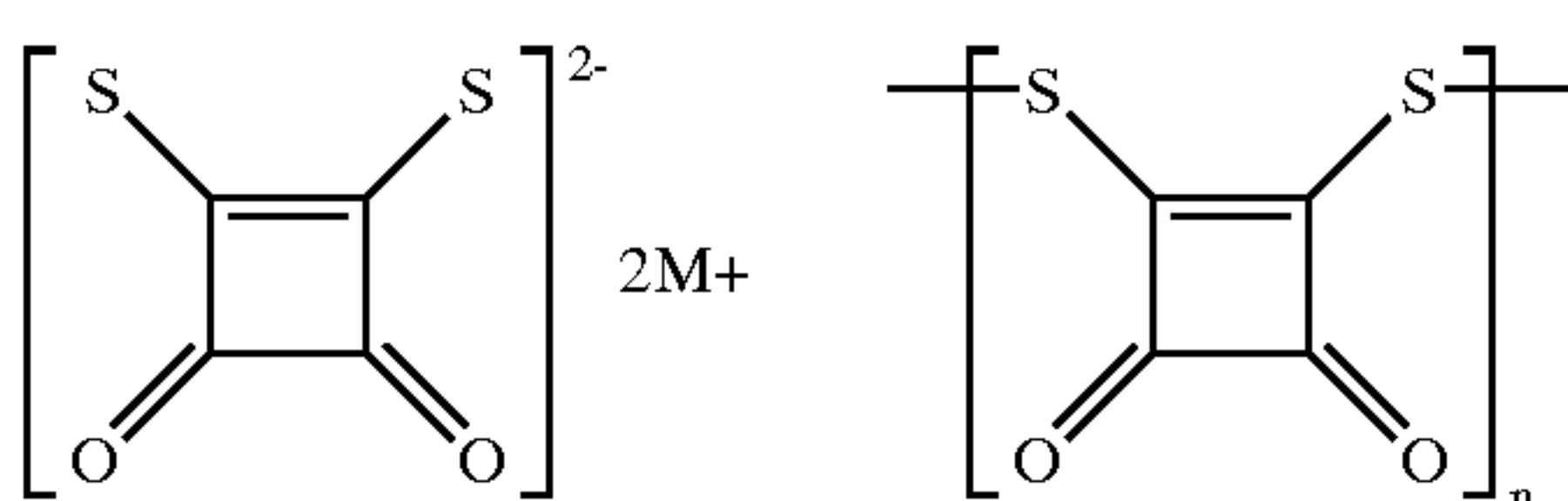
a polymer containing units derived from keto-pyridine represented by the formula



and its oxidation and reduction products;

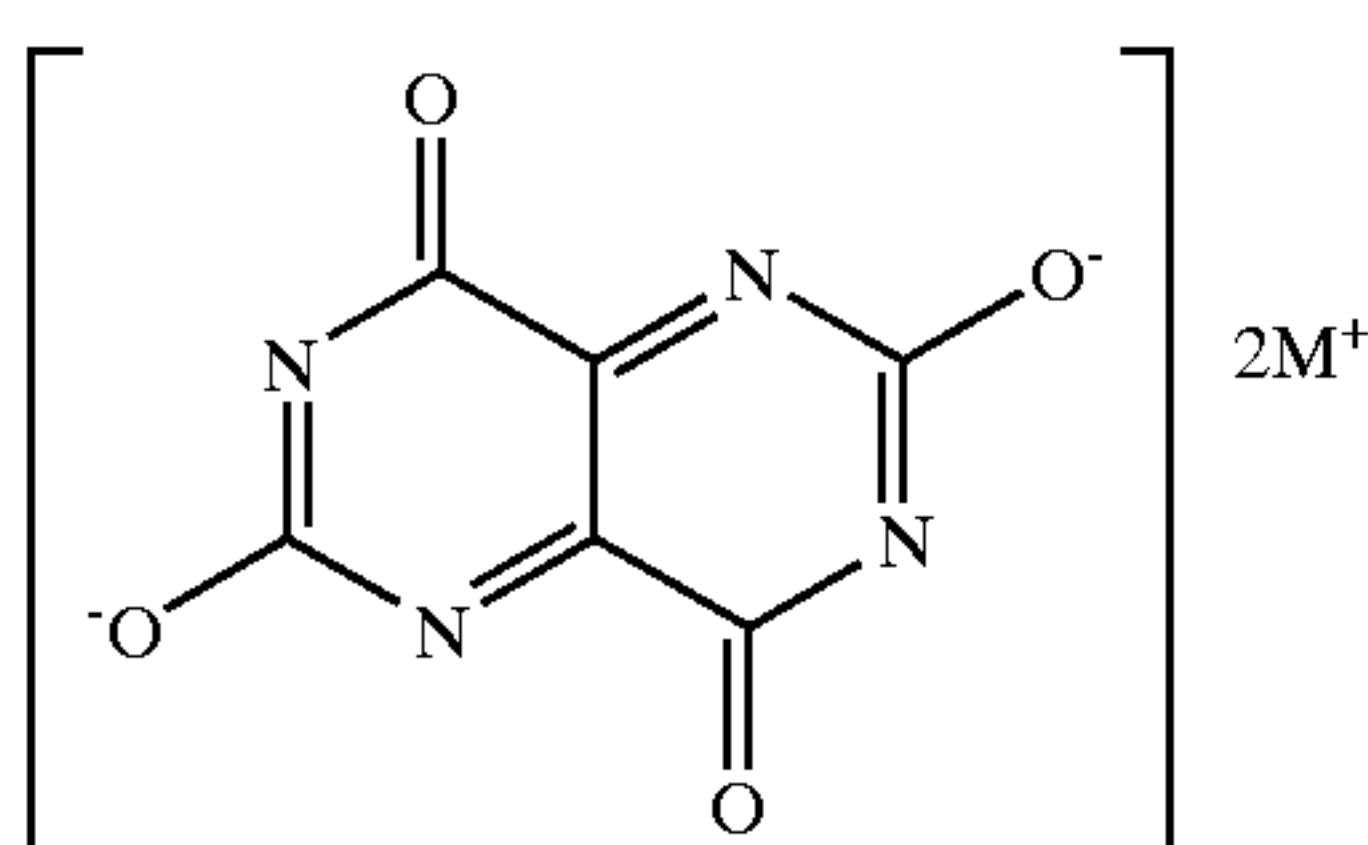
an alternated polymer containing benzoquinone and pyrazine units and their oxidation and reduction products;

a salt of 1,2-dimercaptocyclobutenedione (dithiosquarique) acid and its oxidation compounds, represented by formulae



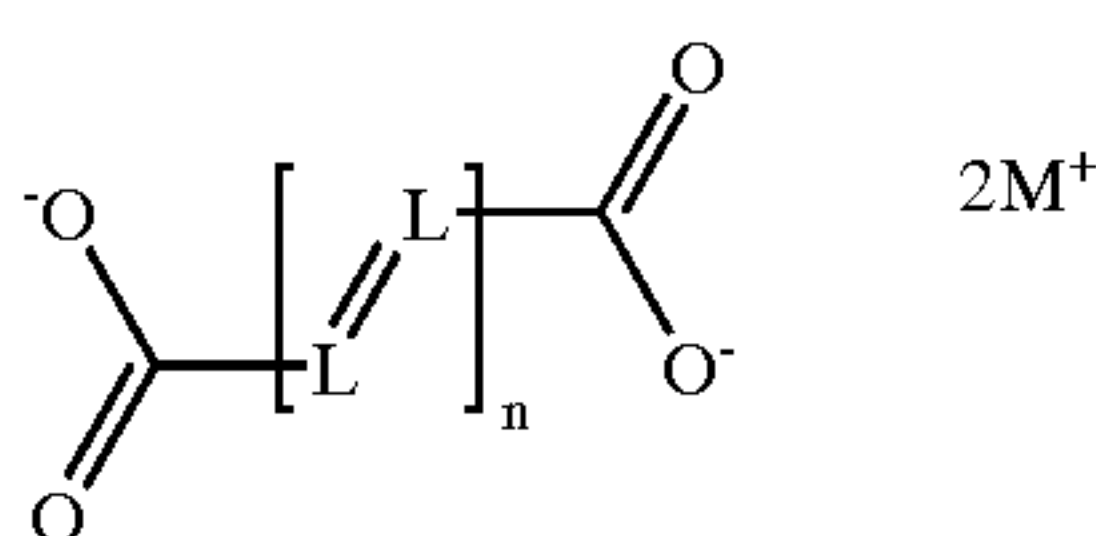
and their products of oxidation;

a salt of 1,5 dihydropyrimido[5,4d]pyrimidine 2,4,6,8(3H, 7H)tetrone represented by the formula



and its oxidation compounds:

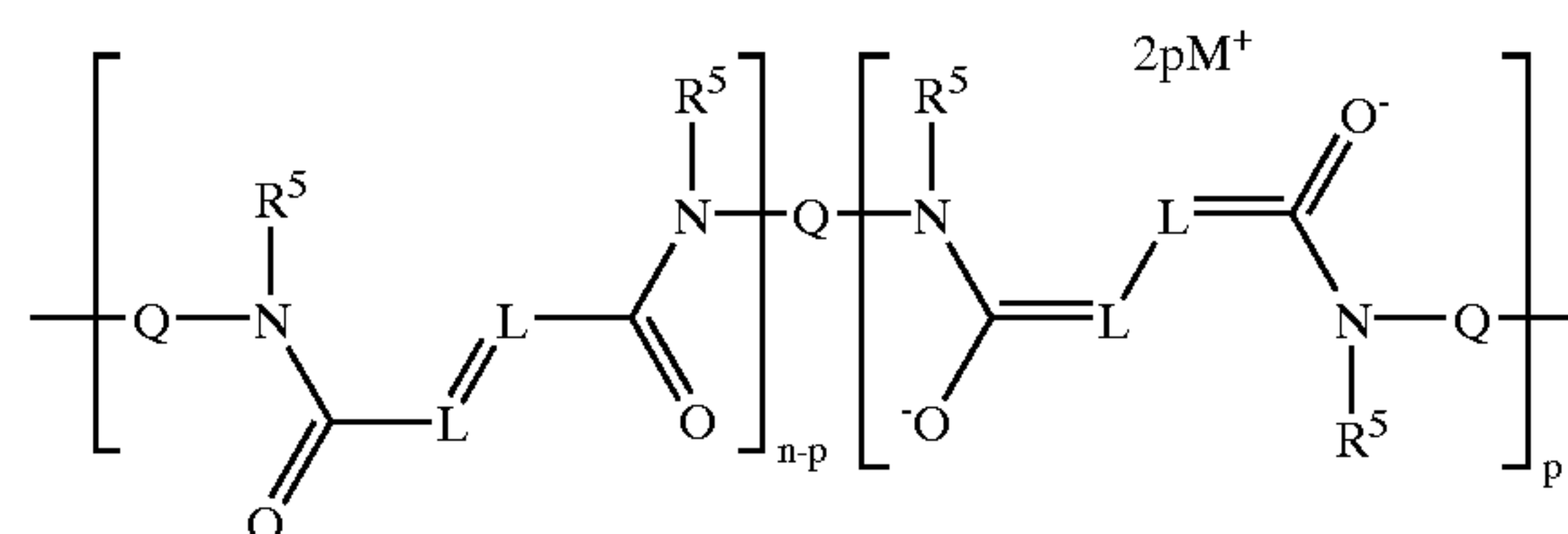
a salt of a dicarboxylic acid comprising groups linked with conjugated segments corresponding to the formula



wherein L is independently CR^5 , N or $C-CN$, and wherein R^5 is hydrogen, C_{1-12} alkyl, C_{2-12} alkenyle,

C_{6-10} aryl, C_{6-10} aryl C_{1-12} alkyl, C_{1-12} alkyl C_{6-10} aryl optionally substituted with one or more oxa, aza or thia of from 1 to 30 carbon atoms, and wherein 2 R^5 can form an aliphatic cycle, an aromatic cycle or a hetero-cycle containing from 4 to 8 carbon atoms when both L are CR^5 ;

a polyamide derived from a dicarboxylic acid comprising groups linked with conjugated segments, corresponding to the formula



wherein L et R^5 are as defined above, and Q is a divalent alkylene, alkenylene, arylene, arylalkylene, alkylarylene of from 1 to 30 carbon atoms optionally containing oxa, aza or thia substituents.

3. Compounds according to claim 2, wherein the rhodizonic acid salt is lithium rhodizionate, potassium rhodizionate or copper rhodizionate, or their reduction products.

4. Compounds according to claim 1, characterized in they are used as a negative electrode component in electrochemical generators when redox couples are comprised between 0.1 and 2 V vs. Li^+/Li° ; or as a positive electrode component in electrochemical generator or as an active or passive electrode in electrochromic devices when redox couples are comprised between 2 et 3.7 V vs. Li^+/Li° .

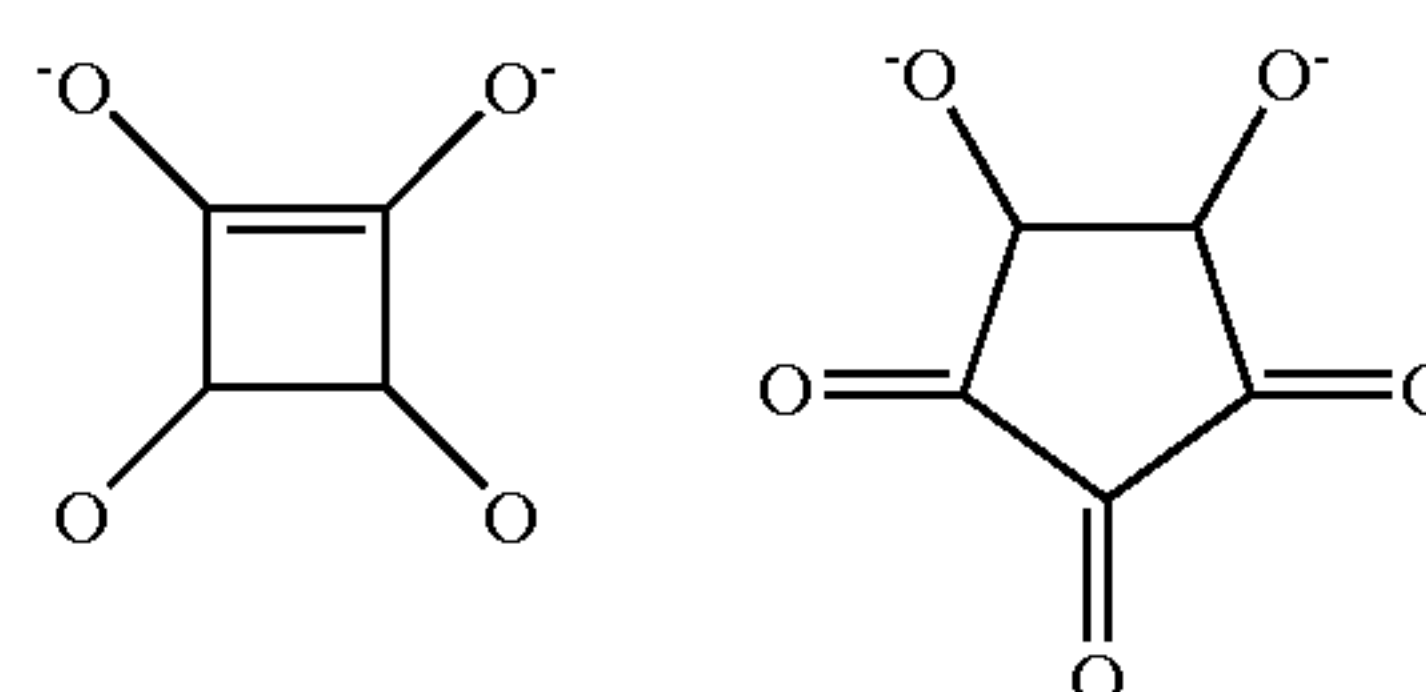
5. A redox electrode material characterized in that it contains, in whole or in part, a compound according to claim 1.

6. A material according to claim 5 characterized in that it furthers contains at least one electronic conductor and at least one binder.

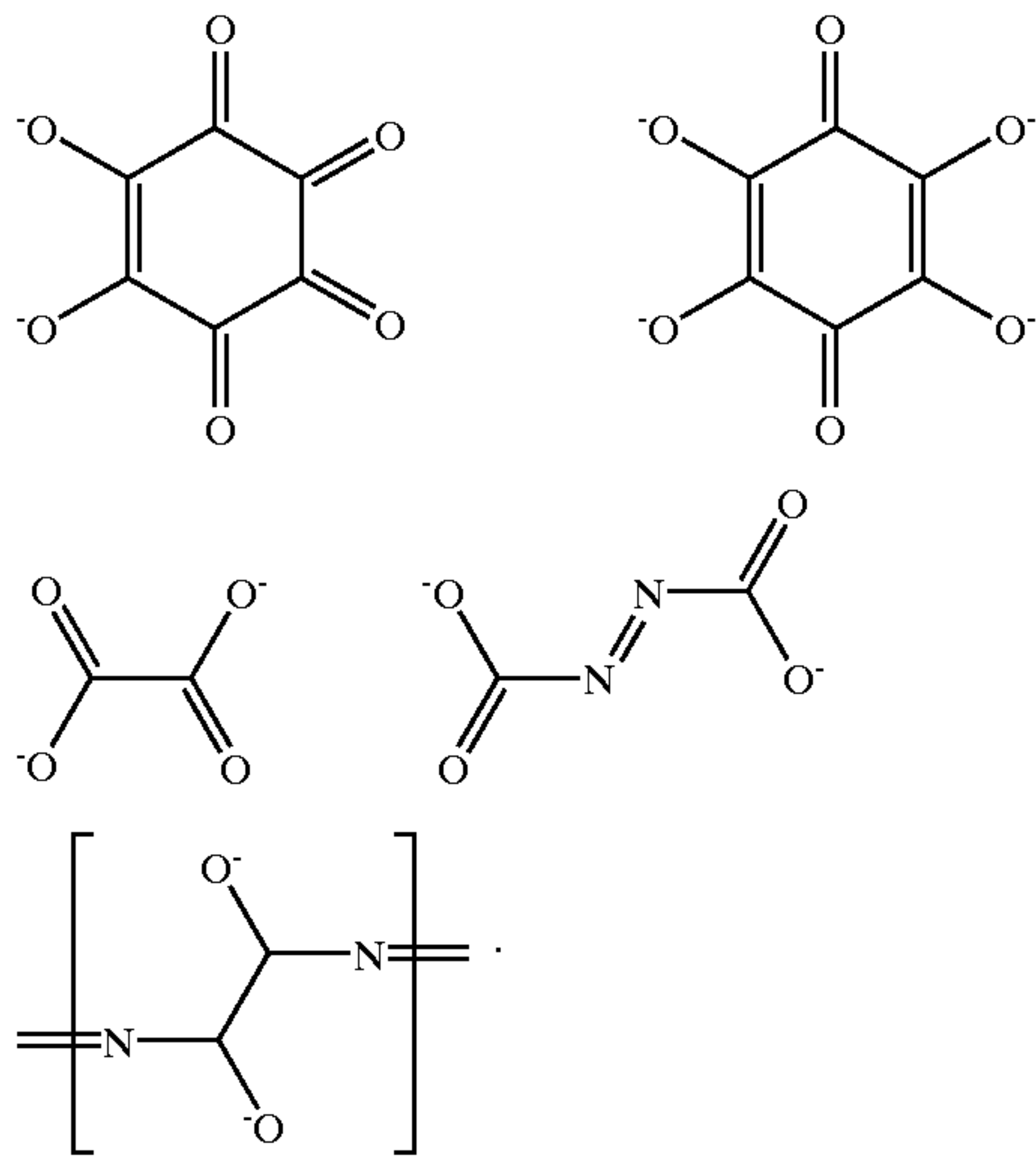
7. A material according to claim 6 wherein the electronic conductor comprises carbon black or graphite powder, and the binder comprises polytetrafluoroethylene, co- or terpolymer of ethylene, propylene and a diene.

8. A material according to claim 5 characterized in that it can be used as a source of lithium to compensate for the inherent losses caused by the formation of passivation layers by the electrodes.

9. A material according to claim 8 characterized in that it comprises derivatives corresponding to the following redox anions:



-continued



10. An electrical energy storage system of the primary or secondary generator-type or super-capacity, comprising an electrolyte, at least one negative electrode and at least one positive electrode comprising a compound according to claim 1.

11. A system according to claim 10 wherein the alkaline cation is lithium cation.

12. A system according to claim 10 characterized in that the negative electrode is metallic lithium or an alloy thereof, optionally in the form of a nanometric dispersion in lithium oxide; double nitrides of lithium and a transition metal; low potential oxides of general formula $\text{Li}_{1+y}\text{Ti}_{2-x/4}\text{O}_4$ wherein x and y vary between 0 et 1; carbon and carbonated products obtained from the pyrolysis of organic materials.

13. A system according to claim 10 wherein the positive electrode comprises a further electrode material compound selected from oxides and sulfides of transition metals.

14. A system according to claim 10 wherein the electrolyte comprises a polar-type polymer, a polar solvent, or mixtures thereof, and at least one ionic salt.

15. A system according to claim 14 wherein the polar-type polymer is a polyether, a vinylidene fluoride-based homo- or copolymer, an acrylonitrile-based homo- or copolymer, or a methyl methacrylate-based homo- or copolymer.

16. A system according to claim 14 wherein the polar solvent comprises acyclic and cyclic carbonates, γ -butyrolactone, monoalkylamides and dialkylamides, tetraalkylsulfamides, dialkyl ether of mono-, di-, tri- et tetraethylene glycols and oligomers of weight inferiors to 2000 g/mole, and mixtures thereof.

* * * * *