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(71) Applicant: **E. I. DU PONT DE NEMOURS AND COMPANY** [US/US]; 1007 Market Street, Wilmington, Delaware 19898 (US).

(72) Inventors: **LIU, Hansan**; 19 Wyndom Cir, Hockessin, Delaware 19707 (US). **LIN, Xiaoping**; 500 Thorndale Drive, Hockessin, Delaware 19707 (US).

(74) Agent: **HALL, William T.**; E. I. du Pont de Nemours and Company, Legal Patent Records Center, Chestnut Run Plaza 721/2640, 974 Centre Road, PO Box 2915 Wilmington, Delaware 19805 (US).

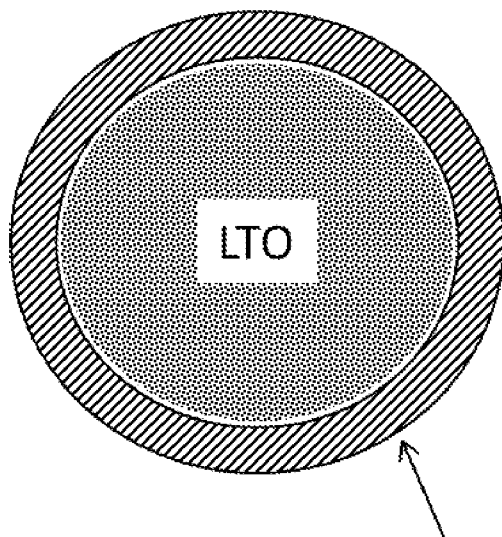
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(54) Title: POLYIMIDE COATED LITHIUM TITANATE PARTICLES AND USE THEREOF IN A LITHIUM ION BATTERY



Polyimide Coating

FIG. 5

(57) Abstract: A coated particle comprising a lithium titanate particle core encased by a polyimide coating, an electrode comprising a plurality of polyimide coated LTO particles an electro-active material, and a lithium ion battery comprising an anode, a cathode, a separator and electrolyte wherein the anode comprises a plurality of polyimide coated LTO particles. The polyimide coating effectively reduces the amount of gas formation typically encountered with use of lithium titanate in electrochemical cells.



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TITLEPOLYIMIDE COATED LITHIUM TITANATE PARTICLES AND USE
THEREOF IN A LITHIUM ION BATTERYTECHNICAL FIELD

10 A coated particle comprising a lithium titanate particle core encased by a polyimide coating, an electrode comprising a plurality of such coated particles as the electro-active material, and a lithium ion battery comprising an electrode comprised of polyimide coated lithium titanate particles.

15

BACKGROUND

Lithium ion batteries (LIB) are becoming increasingly important as energy storage devices and improvements are being aggressively pursued.

20 Carbon is presently the most common anode material for lithium ion batteries, but replacement of carbon with spinel lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$, also referred to as LTO) is being actively investigated due to its many favorable features such as of fast charge-discharge, good safety and long lifetime. However, the commercial success of LIB with LTO is limited in
25 large part because of gas generation during operation, especially at high temperatures ($>45^\circ\text{C}$). The gassing causes increased internal pressure, swelling of pouch-cells, increased impedance, degradation of performance and even safety failure of batteries.

There is still demand however for a LTO based battery without
30 gassing problems.

SUMMARY

In one aspect, there is provided a coated particle comprising a lithium titanate particle core encased by a polyimide coating. The weight
35 percent of polyimide coating is in the range of 0.1% to 5% based on the total weight of polyimide coated particle.

5 In another aspect, there is provided an electrode comprising a plurality of polyimide coated LTO particles as an electro-active material.

 In yet another aspect, there is provided a lithium ion battery comprising an anode, a cathode, a separator and electrolyte wherein the anode comprises a plurality of polyimide coated LTO particles.

10 The polyimide coating effectively reduces the amount of gassing which would otherwise be encountered with lithium titanate in electrochemical cells such as lithium ion batteries.

BRIEF DESCRIPTION OF THE DRAWINGS

15 FIG. 1A is a photograph of LTO powder from example 1 before polyimide coating.

 FIG. 1B is a photograph of LTO powder from example 1 after polyimide coating

 FIG. 2A is a scanning electron micrograph of LTO from example 1
20 before polyimide coating.

 FIG. 2B is a scanning electron micrograph of LTO from example 1 after polyimide coating.

 FIG. 3 is a transmission electron micrograph of a PI coated LTO in cross section.

25 FIG. 4 shows attenuated total reflectance spectra of 2 % PI coated LTO, 1 % PI coated LTO, 1 % PAA coated LTO and uncoated LTO.

 FIG. 5 depicts a cross section of a LTO particle core encased in a polyimide coating.

DESCRIPTION OF EMBODIMENTS

30 “Lithium ion battery” refers to a type of rechargeable battery in which lithium ions move from the anode to the cathode during discharge, and from the cathode to the anode during charge.

 “Anode” refers to the electrode of an electrochemical cell, at which
35 oxidation occurs. In a galvanic cell, such as a battery, the anode is the negatively charged electrode. In a secondary (i.e. rechargeable) battery, the anode is the electrode at which oxidation occurs during discharge and

5 reduction occurs during charging.

“Cathode” refers to the electrode of an electrochemical cell, at which reduction occurs. In a galvanic cell, such as a battery, the cathode is the positively charged electrode. In a secondary (i.e. rechargeable) battery, the cathode is the electrode at which reduction occurs during
10 discharge and oxidation occurs during charging.

The coated particle prescribed herein comprises a lithium titanate particle as the core which is encased by a polyimide coating. Lithium titanate, which is abbreviated herein as ‘LTO’, refers to $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and modified forms thereof. In general, all forms of LTO will have a spinel
15 structure. Modified forms of LTO include ‘doping’ where one or more metals are substituted for some of the lithium and/or titanium atoms within the spinel structure. Modified forms of LTO also include chemical modification of the LTO particle surface (prior to polyimide coating). The LTO, if modified, will retain useful or enhanced properties for use as an
20 electro-active material. In one embodiment, the lithium titanate is unmodified $\text{Li}_4\text{Ti}_5\text{O}_{12}$. In another embodiment the LTO particle surface is modified with Al_2O_3 . In still another embodiment, the LTO particle surface is modified with manganese oxide.

Preparation of lithium titanate and commercial sources thereof are
25 well known to those skilled in the art. Commercial sources of LTO include, for example, LT-105, LT-106 and LT-017 from Ishihara Sangyo Kaisha, LTD, Tokyo, Japan.

The size of the uncoated LTO particles can be any size suitable for use in lithium ion batteries. Typically, however, the LTO particles will have
30 a volume median particle size (D50) in the range of 0.1 μm to 100 μm as measured by standard laser diffraction methods. The polyimide coating is thin and typically does not increase the particle size substantially.

Therefore, a powder consisting of, or consisting essentially of, a plurality of polyimide coated LTO particles will have a particle size distribution about
35 the same as or at most only slightly larger than the starting LTO and will likewise have a volume median particle size in the range of 0.1 μm to 100 μm .

5 The weight percent of polyimide coating is typically between 0.1 % and 5 % based on the total weight of coated LTO particle. In some embodiments, the polyimide coating is in the range of 0.2 wt % to 3 wt % based on the total weight of coated LTO particle. In other embodiments, the polyimide coating is in the range of 0.3 wt % to 2.0 wt % based on the
10 total weight of coated LTO particle. In one embodiment, the weight percent of polyimide coating is an effective amount to reduce gassing of the LTO without severe loss of capacity. An effective amount of polyimide coating reduces gassing by at least 50 % and more preferably at least 70% on a volume basis compared to the amount of gas formed by the
15 same LTO without the polyimide coating. Preferably an effective amount of polyimide coating will cause no more than 15% loss of capacity, preferably no more than 10% loss of capacity and even more preferably no more than 5 % loss of capacity compared to the same LTO without polyimide coating. It will be appreciated that the effective amount of
20 polyimide coating can vary depending on the characteristics of the starting LTO, for example particle size and surface area.

 The polyimide is not limited and can be any suitable polyimide composition. The method of forming the polyimide coating is not limited, but will typically comprise coating the LTO with polyamic acid ("precursor")
25 composition and curing (or "imidizing") the polyamic acid to polyimide. The terms "precursor" or "polyamic acid" are used interchangeably and are intended to mean a relatively low molecular weight polyamic acid solution. The solution can be in any fluid form, such as a slurry, dispersion, or solution. The precursor solution can comprise a solvent which can be any
30 solvent that is inert to the polyamic acid, but is typically the solvent used in the preparation of the polyamic acid. Imidization of the polyamic acid can be accomplished, for example, by dehydration at elevated temperature according to methods well known in the art.

 Polyamic acid is the reaction product of a tetracarboxylic acid
35 dianhydride and an organic diamine. In one embodiment the dianhydride is aromatic, in another embodiment the diamine is aromatic, and in another embodiment both the dianhydride and the diamine are aromatic.

5 The polyamic acids can be prepared by any suitable method, such as those discussed in Polyimides (Encyclopedia of Polymer Science and Technology, RG Bryant, 2006, DOI: 10.1002/0471440264.pst272.pub2, John Wiley & Sons, Inc.). One method includes dissolving the diamine in a dry solvent and slowly adding the dianhydride under conditions of agitation
10 and controlled temperature, and in a dry atmosphere, such as nitrogen.

Suitable organic dianhydrides include, but are not limited to, pyromellitic dianhydride (PMDA); biphenyltetracarboxylic dianhydride (BPDA); 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA); 2,3,6,7-naphthalene tetracarboxylic dianhydride; 3,3',4,4'-
15 tetracarboxybiphenyl dianhydride; 1,2,5,6-tetracarboxynaphthalene dianhydride; 2,2',3,3'-tetracarboxybiphenyl dianhydride; 2,2-bis(3,4-dicarboxyphenyl) propane dianhydride; bis(3,4-dicarboxyphenyl) sulfone dianhydride; bis(3,4-dicarboxyphenyl) ether dianhydride; naphthalene-1,2,4,5-tetracarboxylic dianhydride; naphthalene-1,4,5,8-tetracarboxylic
20 dianhydride; pyrazine-2,3,5,6-tetracarboxylic dianhydride; 2,2-bis(2,3-dicarboxyphenyl) propane dianhydride; 1,1-bis(2,3-dicarboxyphenyl) ethane dianhydride; 1,11-bis(3,4-dicarboxyphenyl) ethane dianhydride; bis(2,3-dicarboxyphenyl) methane dianhydride; bis(3,4-dicarboxyphenyl) methane dianhydride; benzene-1,2,3,4-tetracarboxylic dianhydride;
25 3,4,3',4'-tetracarboxybenzophenone dianhydride; perylene-3,4,9,10-tetracarboxylic dianhydride; bis-(3,4-dicarboxyphenyl) ether tetracarboxylic dianhydride; 4,4'-oxydiphthalic anhydride; 3,3',4,4'-diphenyl sulfone tetracarboxylic dianhydride; 2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane; Bisphenol A dianhydride (4,4'-(4,4'-
30 isopropylidenediphenoxy)bis(phthalic anhydride)); and mixtures thereof. In one embodiment the organic dianhydrides is pyromellitic dianhydride, 3,3',4,4'-biphenyl tetracarboxylic dianhydride, 3,3',4,4'-benzophenone tetracarboxylic dianhydride, 4,4'-oxydiphthalic anhydride, 3,3',4,4'-diphenyl sulfone tetracarboxylic dianhydride, 2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane, Bisphenol A dianhydride, or mixtures thereof.
35

Suitable organic diamines include, but are not limited to, oxydianiline (ODA), 3,4'-oxydianiline, 1,3-bis-(4-aminophenoxy) benzene,

- 5 4,4'-oxydianiline, 1,4-diaminobenzene, 1,3-diaminobenzene, 2,2'-bis(trifluoromethyl) benzidine, 4,4'-diaminobiphenyl, 4,4'-diaminodiphenyl sulfide, 9,9'-bis(4-amino)fluorene, 1,3-bis(4-aminophenoxy)benzene (RODA), and 1,4 phenylenediamine (PDA); m-phenylenediamine; p-phenylenediamine; 4,4'-diaminodiphenyl propane; 4,4'-diaminodiphenyl
- 10 methane benzidine; 4,4'-diaminodiphenyl sulfide; 4,4'-diaminodiphenyl sulfone; 4,4'-diaminodiphenyl ether; 1,5-diaminonaphthalene; 3,3'-dimethyl benzidine; 3,3'-dimethoxy benzidine; bis-(para-beta-amino-t-butylphenyl)ether; 1-isopropyl-2,4-m-phenylenediamine; m-xylylenediamine; p-xylylenediamine; di(paraminocyclohexyl) methane;
- 15 hexamethylenediamine; heptamethylenediamine; octamethylenediamine; decamethylenediamine; nonamethylenediamine; 4,4'-dimethylheptamethylenediamine-2,11-diaminododecane; 1,2-bis(3-aminopropoxyethane); 2,2-dimethylpropylenediamine; 3-methoxyhexamethylenediamine; 2,5-dimethyl hexamethylenediamine; 3-
- 20 methylheptamethylenediamine; piperazine; 1,4-diamino cyclohexane; 1,12-diamino octadecane; 2,5-diamino-1,3,4-thiadiazole; 2,6-diaminoanthraquinone; 9,9'-bis(4-aminophenyl fluorene); p,p'-4,4-bis(aminophenoxy); 5,5'-diamino-2,2'-bipyridylsulfide; 2,4-diaminoisopropyl benzene; 1,3-diaminobenzene (MPD); 2,2'-
- 25 bis(trifluoromethyl) benzidine; 4,4'-diaminobiphenyl; 4,4'-diaminodiphenyl sulfid; 9,9'-bis(4-amino)fluorene; and mixtures thereof. In one embodiment the organic diamine is 3,4'-oxydianiline, 1,3-bis-(4-aminophenoxy)benzene, 4,4'-oxydianiline, 1,4-diaminobenzene, 1,3-diaminobenzene, 2,2'-bis(trifluoromethyl) benzidine, 4,4'-diaminobiphenyl, 4,4'-
- 30 diaminodiphenyl sulfide, 9,9'-bis(4-amino)fluorene or mixtures thereof.

In one embodiment the aromatic dianhydride is pyromellitic dianhydride (PMDA), and the aromatic diamine is oxydianiline (ODA).

- Any suitable aprotic polar solvent can be used in the synthesis of polyamic acid. Exemplary solvents for polyamic acid include N,N-
- 35 dimethylformamide, N,N-dimethylacetamide (DMAC), N,N-diethylformamide (DMF), N,N-diethylacetamide, N,N-

- 5 dimethylmethoxyacetamide, N-methyl-2-pyrrolidone, N-methylcaprolactam, and the like.

Polyimide precursor is readily available from commercial sources well known to those skilled in the art, for example, HD Microsystems, Parlin, New Jersey.

- 10 The LTO can be coated with precursor by any suitable coating process. Such processes are well known to those skilled in the art. Generally, a solution of polyimide precursor (polyamic acid) in suitable solvent is applied to the LTO particles so that the surface of the particles is evenly and completely coated with the polyamic acid solution. The solvent
15 is then removed and the dried particles are heated to convert (cure) the polyamic acid to polyimide. The presence of polyimide on the surface of the LTO can be detected by standard techniques such as infrared spectroscopy.

- In one embodiment, a coated particle of LTO is coated with
20 polyimide which comprises, consists essentially of, or consists of monomers pyromellitic dianhydride and oxydianiline.

- The coated LTO is advantageous as an electro-active material and can be formed into an electrode according to methods well known in the art. Electrode ingredients typically include the electro-active material,
25 such as coated LTO according to this invention, a conductive agent and a binder. Commonly, the electrode ingredients are mixed with solvent and formed into a paste which is cast onto a current collector. The solvent is then removed and the dried electrode is formed into the desired size and shape. The electrode may further comprise other ingredients known in the
30 art.

- The conductive agent provides conductivity to the electrode and may be any one of various materials that do not cause any deleterious effects and that conduct electrons. Examples of the conductive agent include a carbonaceous material, such as natural graphite, artificial
35 graphite, flaky graphite, carbon black, acetylene black, ketjen black, denka black, carbon fiber, carbon nanotube or graphene; a metallic material, such as copper powder or fiber, nickel powder or fiber, aluminum powder

- 5 or fiber, or silver powder or fiber; a conductive polymer such as a polyphenylene derivative, and mixtures thereof.

The binder may allow active material particles to be attached to each other and the electro-active material to be attached to a current collector. Non-limiting examples of the binder include polyvinylalcohol,
10 carboxymethylcellulose, hydroxypropylcellulose, diacetylcellulose, polyvinylchloride, carboxylated polyvinylchloride, polyvinylfluoride, an ethylene oxide-containing polymer, polyvinylpyrrolidone, polyurethane, polytetrafluoroethylene, polyvinylidene fluoride, polyethylene, polypropylene, styrene-butadiene rubber, acrylated styrene-butadiene
15 rubber, epoxy resin, nylon, and a mixture thereof. For example, the binder may be polyvinylidene fluoride (PVDF). The binder will typically be present in an amount of from 5 wt % to 10 wt % based on the weight of electro-active material.

The solvent used to make the electrode paste can be any one of
20 various solvents commonly used for such purpose. Examples of the solvent include a chain carbonate such as dimethyl carbonate, ethyl methyl carbonate, diethyl carbonate or dipropyl carbonate, a cyclic carbonate such as ethylene carbonate, propylene carbonate or butylene carbonate, dimethoxyethane, diethoxyethane, a fatty acid ester derivative,
25 gamma-butyrolactone, N-methylpyrrolidone (NMP), acetone, or water. The solvent may also be a combination of two or more of these.

The "current collector" refers to a structural part of an electrode assembly whose primary purpose is to conduct electricity between the actual working part of the electrode, and the terminals of an
30 electrochemical cell. The current collector material may be any one of various materials commonly used in the art, for example, a copper foil or an aluminum foil, but is not limited thereto.

An electrode comprising coated LTO is advantageous for use in an electrochemical cell. In some embodiments, the electrochemical cell is a
35 lithium battery. In some embodiments, the lithium ion battery comprises an anode, a cathode, a separator between the cathode and anode, an electrolyte, and a housing to enclose the battery.

5 As prescribed herein, the anode is an electrode comprising polyimide coated LTO. The cathode, is an electrode comprising suitable cathode-active material. The cathode-active material is any suitable electro-active material which can be advantageously paired with the polyimide coated LTO anode. The electrode comprising suitable cathode-active material can be formed in the same way as described herein before.

Suitable electro-active cathode materials include electro-active transition metal oxides comprising lithium, such as LiCoO_2 , LiNiO_2 , LiMn_2O_4 , or LiV_3O_8 ; oxides of layered structure such as $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ where $x+y+z$ is about 1, $\text{LiCo}_{0.2}\text{Ni}_{0.2}\text{O}_2$, $\text{Li}_{1+z}\text{Ni}_{1-x-y}\text{Co}_x\text{Al}_y\text{O}_2$ where $0 < x < 0.3$, $0 < y < 0.1$, olivine structured LiFePO_4 , LiMnPO_4 , LiCoPO_4 , and LiVPO_4F ; spinel structured $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$; mixed metal oxides of cobalt, manganese, and nickel such as those described in U.S. Patent No. 6,964,828 and U.S. Patent No. 7,078,128; nanocomposite cathode compositions such as those described in U.S. Patent No. 6,680,145; lithium-rich layered-layered composite cathodes such as those described in U.S. Patent No. 7,468,223; and cathodes such as those described in U.S. Patent No. 7,718,319 and the references therein.

Another suitable electro-active material is a lithium-containing manganese composite oxide having a spinel structure as an electro-active cathode material. A lithium-containing manganese composite oxide suitable for use herein comprises oxides of the formula $\text{Li}_x\text{Ni}_y\text{M}_z\text{Mn}_{2-y-z}\text{O}_{4-d}$, wherein x is 0.03 to 1.0; x changes in accordance with release and uptake of lithium ions and electrons during charge and discharge; y is 0.3 to 0.6; M comprises one or more of Cr, Fe, Co, Li, Al, Ga, Nb, Mo, Ti, Zr, Mg, Zn, V, and Cu; z is 0.01 to 0.18; and d is 0 to 0.3. In one embodiment in the above formula, y is 0.38 to 0.48, z is 0.03 to 0.12, and d is 0 to 0.1. In one embodiment in the above formula, M is one or more of Li, Cr, Fe, Co and Ga. Stabilized manganese cathodes may also comprise spinel-layered composites which contain a manganese-containing spinel component and a lithium rich layered structure, as described in U.S. Patent No. 7,303,840.

Other suitable electro-active include layered oxides such as LiCoO_2 or $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ where $x+y+z$ is about 1, that can be charged to cathode

5 potentials higher than the standard 4.1 to 4.25 V range in order to access higher capacity. Other examples are layered-layered high-capacity oxygen-release cathodes such as those described in U.S. Patent No. 7,468,223 charged to upper charging voltages above 4.5 V.

The separator is porous and serves to prevent short circuiting
10 between the anode and the cathode. The porous separator typically consists of a single-ply or multi-ply sheet of a microporous polymer such as polyethylene, polypropylene, polyamide or polyimide, or a combination thereof. The pore size of the porous separator is sufficiently large to permit transport of ions to provide ionically conductive contact between the anode
15 and cathode, but small enough to prevent contact of the anode and cathode either directly or from particle penetration or dendrites which can form on the anode and cathode. Examples of porous separators suitable for use herein are disclosed in U.S. Patent Application Publication No. 2012/0149852.

20 "Electrolyte composition" as used herein, refers to a chemical composition suitable for use as an electrolyte in an electrochemical cell. An electrolyte composition typically comprises at least one solvent and at least one electrolyte salt.

"Electrolyte salt" as used herein, refers to an ionic salt that is at
25 least partially soluble in the solvent of the electrolyte composition and that at least partially dissociates into ions in the solvent of the electrolyte composition to form a conductive electrolyte composition.

Typically, the electrolyte solvent comprises one or more alkyl carbonates including, for example, any one or a mixture of ethylene
30 carbonate (EC), ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC).

Suitable solvents for electrolyte compositions can also include fluorinated acyclic carboxylic acid esters, represented by the formula $R^1-COO-R^2$, where R^1 and R^2 independently represent an alkyl group, the
35 sum of carbon atoms in R^1 and R^2 is 2 to 7, at least two hydrogens in R^1 and/or R^2 are replaced by fluorines and neither R^1 nor R^2 contains a FCH_2 or FCH group. Examples of suitable fluorinated acyclic carboxylic acid

5 esters include without limitation $\text{CH}_3\text{-COO-CH}_2\text{CF}_2\text{H}$ (2,2-difluoroethyl acetate, CAS No. 1550-44-3), $\text{CH}_3\text{-COO-CH}_2\text{CF}_3$ (2,2,2-trifluoroethyl acetate, CAS No. 406-95-1), $\text{CH}_3\text{CH}_2\text{-COO-CH}_2\text{CF}_2\text{H}$ (2,2-difluoroethyl propionate, CAS No. 1133129-90-4), $\text{CH}_3\text{-COO-CH}_2\text{CH}_2\text{CF}_2\text{H}$ (3,3-difluoropropyl acetate), $\text{CH}_3\text{CH}_2\text{-COO-CH}_2\text{CH}_2\text{CF}_2\text{H}$ (3,3-difluoropropyl propionate), and $\text{HCF}_2\text{-CH}_2\text{-CH}_2\text{-COO-CH}_2\text{CH}_3$ (ethyl 4,4-difluorobutanoate, CAS No. 1240725-43-2). In one embodiment, the fluorinated acyclic carboxylic acid ester is 2,2-difluoroethyl acetate ($\text{CH}_3\text{-COO-CH}_2\text{CF}_2\text{H}$).

Other suitable fluorinated acyclic carbonates are represented by the
15 formula $\text{R}^3\text{-OCOO-R}^4$, where R^3 and R^4 independently represent an alkyl group, the sum of carbon atoms in R^3 and R^4 is 2 to 7, at least two hydrogens in R^3 and/or R^4 are replaced by fluorines and neither R^3 nor R^4 contains a FCH_2 or FCH group. Examples of suitable fluorinated acyclic carbonates include without limitation $\text{CH}_3\text{-OC(O)O-CH}_2\text{CF}_2\text{H}$ (methyl 2,2-difluoroethyl carbonate, CAS No. 916678-13-2), $\text{CH}_3\text{-OC(O)O-CH}_2\text{CF}_3$ (methyl 2,2,2-trifluoroethyl carbonate, CAS No. 156783-95-8),

$\text{CH}_3\text{-OC(O)O-CH}_2\text{CF}_2\text{CF}_2\text{H}$ (methyl 2,2,3,3-tetrafluoropropyl carbonate, CAS No. 156783-98-1), $\text{HCF}_2\text{CH}_2\text{-OCOO-CH}_2\text{CH}_3$ (ethyl 2,2-difluoroethyl carbonate, CAS No. 916678-14-3), and $\text{CF}_3\text{CH}_2\text{-OCOO-CH}_2\text{CH}_3$ (ethyl 2,2,2-trifluoroethyl carbonate, CAS No. 156783-96-9).

Other suitable fluorinated acyclic ethers are represented by the formula: $\text{R}^5\text{-O-R}^6$, where R^5 and R^6 independently represent an alkyl group, the sum of carbon atoms in R^5 and R^6 is 2 to 7, at least two hydrogens in R^5 and/or R^6 are replaced by fluorines and neither R^5 nor R^6
30 contains a FCH_2 or FCH group. Examples of suitable fluorinated acyclic ethers include without limitation $\text{HCF}_2\text{CF}_2\text{CH}_2\text{-O-CF}_2\text{CF}_2\text{H}$ (CAS No. 16627-68-2) and $\text{HCF}_2\text{CH}_2\text{-O-CF}_2\text{CF}_2\text{H}$ (CAS No. 50807-77-7).

A mixture of two or more of these fluorinated acyclic carboxylic acid ester, fluorinated acyclic carbonate, and/or fluorinated acyclic ether
35 solvents may also be used. Other suitable mixtures can include anhydrides. One suitable electrolyte solvent mixture includes a fluorinated acyclic carboxylic acid ester, ethylene carbonate, and maleic anhydride,

5 such as 2,2-difluoroethyl acetate, ethylene carbonate, and maleic anhydride. The electrolyte composition can comprise about 61 % 2,2-difluoroethyl acetate, about 26 % ethylene carbonate, and about 1 % maleic anhydride by weight of the total electrolyte composition.

The electrolyte compositions described herein can also contain at
 10 least one electrolyte salt. Suitable electrolyte salts include without limitation

lithium hexafluorophosphate (LiPF_6),
 lithium tris(pentafluoroethyl)trifluorophosphate ($\text{LiPF}_3(\text{C}_2\text{F}_5)_3$),
 lithium bis(trifluoromethanesulfonyl)imide,
 15 lithium bis(perfluoroethanesulfonyl)imide,
 lithium (fluorosulfonyl) (nonafluorobutanesulfonyl)imide,
 lithium bis(fluorosulfonyl)imide,
 lithium tetrafluoroborate,
 lithium perchlorate,
 20 lithium hexafluoroarsenate,
 lithium trifluoromethanesulfonate,
 lithium tris(trifluoromethanesulfonyl)methide,
 lithium bis(oxalato)borate,
 lithium difluoro(oxalato)borate,
 25 $\text{Li}_2\text{B}_{12}\text{F}_{12-x}\text{H}_x$ where x is equal to 0 to 8, and
 mixtures of lithium fluoride and anion receptors such as
 $\text{B}(\text{OC}_6\text{F}_5)_3$.

Mixtures of two or more of these or comparable electrolyte salts may also be used. A suitable electrolyte salt is lithium
 30 hexafluorophosphate. The electrolyte salt can be present in the electrolyte composition in an amount of about 0.2 to about 2.0 M, or about 0.3 to about 1.5 M, or about 0.5 to about 1.2 M.

The optimum range of salt and solvent concentrations in the electrolyte may vary according to specific materials being employed and
 35 the anticipated conditions of use, for example, according to the intended operating temperature. In one embodiment, the solvent is 20 to 40 parts

5 by volume of ethylene carbonate and 60 to 80 parts by volume of ethyl methyl carbonate, and the salt is LiPF_6 .

Alternatively, the electrolyte may comprise a lithium salt such as, lithium hexafluoroarsenate, lithium bis-trifluoromethyl sulfonamide, lithium bis(oxalate)boronate, lithium difluorooxalatoboronate, or the Li^+ salt of
10 polyfluorinated cluster anions, or combinations of these. Alternatively, the electrolyte may comprise a solvent, such as, propylene carbonate, esters, ethers, or trimethylsilane derivatives of ethylene glycol or poly(ethylene glycols) or combinations of these. Additionally, the electrolyte may contain various additives known to enhance the performance or stability of Li-ion
15 batteries, as reviewed for example by K. Xu in Chem. Rev., 104, 4303 (2004), and S.S. Zhang in J. Power Sources, 162, 1379 (2006).

The housing of the electrochemical cell may be any suitable container to house the electrochemical cell components described above. Such a container may be fabricated in the shape of a cylindrical battery, a
20 rectangular battery, a coin-type battery, or a pouch-type battery; and according to a size, a bulky battery and a thin-film type battery. Methods of manufacturing the lithium secondary batteries as described above are widely known in the art.

The electrochemical cell or lithium ion battery disclosed herein may
25 be used for grid storage or as a power source in various electronically-powered or -assisted devices ("electronic device") such as a transportation device (including a motor vehicle, automobile, truck, bus or airplane), a computer, a telecommunications device, a camera, a radio or a power tool.

30

EXAMPLES

It is understood that the embodiments described herein disclose only illustrative but not exhaustive examples of the invention set forth.

35

Materials

5 Poly(amic acid) was PI-2454, a 13 wt % solution comprised of
pyromellitic dianhydride/oxydianiline polymer obtained from HD
Microsystem Inc, Parlin, New Jersey, USA. N-methyl-2-pyrrolidone
(NMP), anhydrous, was obtained from Sigma-Aldrich. Conductive carbon,
Super C65, was obtained from Timcal Ltd, Bodio, CH. Polyvinylidene
10 fluoride (PVDF), KF#9130, 13 wt % in NMP, was obtained from Kureha
America, New York, NY, USA. Ethylene carbonate (EC) and ethyl methyl
carbonate (EMC) were obtained from Novolyte Technologies/BASF.
Lithium foil, 0.75 mm thick, was obtained from Alfa Aesar. Separator,
Celgard 2500, a monolayer polypropylene film, was obtained from Celgard
15 LLC, Charlotte, North Carolina, USA. Graphite powder, CPreme® G8, was
obtained from ConocoPhillips Specialty Products, Inc, Houston, Texas,
USA.

Lithium titanate was prepared according to methods described in
co-pending U.S. Patent Application No. 13/910230. The BET surface area
20 was 3.9 m²/g. The pore volume was 0.0071 mL/g. The volume median
particle size, D50, was 18.39 µm, the D10 was 1.95 µm and the D90 was
34.06 µm as determined by laser diffraction techniques (Horiba LA910).

Example 1

25 Preparation of 1 % PI Coated LTO

LTO, 20 g, and poly(amic acid), 20 g of 1.0 wt % solution of PI2454
in NMP, were combined in a wide-mouth glass jar and mixed with a
planetary centrifugal mixer (Thinky ARE-310) for one minute at 2000 rpm.
30 The mixture was then sonicated in an ultrasonic water bath for an hour at
room temperature and stirred for an additional 12 hours with a magnetic
stirrer at room temperature. The solvent was removed from the mixture by
distillation at about 100 °C for about 60 minutes and then heating in a
vacuum oven at 80 °C for 12 hours to yield poly(amic) acid coated LTO.
35 The poly(amic) acid coating was cured to polyimide by heating the
poly(amic) acid coated LTO under inert atmosphere (argon) according to
the following conditions: (1) purge with argon gas at 25 °C for one hour;

- 5 (2) increase the temperature from 25 °C to 150 °C over one hour (2 °C/minute); (3) hold at 150 °C for 30 minutes; (4) Increase the temperature from 150 °C to 230 °C in 40 minutes (2 °C/minute); (5) hold at 230 °C for 30 minutes; (6) increase the temperature from 230 °C to 300 °C in 35 minutes (2 °C/minute); (7) hold the mixture at 300 °C for 30 minutes; (8)
- 10 Increase the temperature from 300 °C to 400 °C in 50 minutes (2 °C/minute); (9) hold at 400 °C for 30 minutes.

The coated LTO thus obtained was calculated to have a 0.99 wt % PI coating (rounded to 1 wt % for ease of reference) based on the total weight of coated LTO. The calculation is based on the weight ratio of

15 polyamic acid to LTO initially added and assumes substantially all of the polyamic acid is converted to polyimide.

FIG. 1A shows a photograph of LTO before PI coating and FIG. 1B shows a photo of LTO after 1 % PI coating. Both are free flowing powders.

20 FIG. 2A shows a scanning electron micrograph (SEM) of LTO particles before PI coating and FIG. 2B shows an SEM of LTO particles after 1 % PI coating.

FIG. 3 shows a transmission electron micrograph (TEM) of the 1% PI coated LTO particle in cross section where the thin layer of PI can be

25 seen on the LTO surface.

Example 2

Preparation of 2 % PI Coated LTO

30 A polyimide coated LTO was prepared following the same procedure as Example 1 except the 20 g of poly(amic acid) solution initially added was 2.0 wt % of poly(amic acid). The weight percent of PI was 1.96 wt % (rounded to 2 wt % for ease of reference) based on the total weight of coated LTO.

35

Example 3

Preparation of 3 % PI Coated LTO

5

A polyimide coated LTO was prepared following the same procedure as Example 1 except the 20 g of poly(amic acid) solution initially added was 3.0 wt % of poly(amic acid). The final weight percent of PI coating was calculated to be 2.91 wt % (rounded to 3 wt % for ease of reference) based on the total weight of coated LTO.

Example 4 ATR Spectra of Coated LTO

FIG. 4 shows ATR (Attenuated Total Reflectance) spectra of 1 % PI coated LTO and 2 % PI coated LTO. For comparison, also shown are scans for uncoated LTO and 1 % poly(amic acid) ("PAA") coated LTO before curing. The samples were run on a Nicolet 6700 FTIR (ThermoFisher Scientific) with a Golden Gate diamond ATR unit (Specac).

The major bands for polyimide are imide absorption bands near 1720 cm^{-1} (C=O symmetrical stretching), 1780 cm^{-1} (C=O asymmetrical stretching), and 1380 cm^{-1} (C-N stretching). Other bands overlap with poly(amic acid). The results clearly confirm that coating is present on the LTO surface and that polyimide was formed after curing.

FIG. 5 depicts, in cross section, a LTO particle core encased in a polyimide coating. The relative thickness of the coating is not necessarily to scale.

Example 5 Electrode Preparation with PI Coated LTO

The LTO active materials and conductive carbon were dried in a vacuum oven at $120\text{ }^{\circ}\text{C}$ for 12 hours prior to use. The active material (0.7920 g) and conductive carbon (0.0990 g) were combined in a glass vial and mixed in a Spex mixer for 30 minutes before adding NMP (1.3475 g) and PVDF solution (0.7615g of a 13 % PVDF solution in NMP) to form an electrode paste with a solid content of 33 wt % and a ratio of

- 5 carbon/PVDF/active material of 10/10/80. Glass beads (6 pieces, 4 mm diameter) were added to the paste which was then thoroughly mixed in the Spex mixer, stopping periodically to limit heat build-up.

To prepare the electrode, a clean glass plate (18 cm by 13 cm) with Kapton® tape on the edges (2 cm wide, 95 µm thick), was placed on top of
10 a vacuum hold down plate (30 cm x 23 cm). A piece of copper foil was then placed on the glass plate and held down by surface tension of a small amount of IPA put on the glass before copper film placement. The electrode paste was spread on the foil with a doctor-blade at a constant speed using the gate of 5 mils (0.005 inch, 0.125 mm) to form a film which
15 was dried for 30 minutes at 120 °C under nitrogen flow. The film was further dried at 120 °C under vacuum for 10 hour and then allowed to cool to room temperature under vacuum. The dried film was pressed by a calendar machine (Design Prove Machine, Canada) under about 590 psi (4068 kPa) at a rotational speed of 1.25 rpm and ambient room
20 temperature to densify the film and form the prepared electrode. In this way, an electrode with each of 1 %, 2 % and 3 % polyimide coated LTO from Examples 1-3 was made.

Comparative Example A

25 Electrode Preparation with Uncoated LTO

In the same manner as Example 5, an electrode was prepared using uncoated LTO in place of the coated LTO.

30 Comparative Example B

Electrode Preparation with Uncoated LTO and PI Binder

Using the general procedure of Example 5, an electrode was prepared with uncoated LTO as the electro-active material and polyimide
35 as the binder replacing PVDF. Poly(amic acid) (9.8485 g of 13 % NMP solution) was mixed with LTO (2.6 g), carbon black (0.325 g, C65) and NMP (0.2265 g) to form a paste with a ratio of LTO:Carbon:PI (80:10:10).

- 5 The paste was cast onto the copper foil. To cure the polyamic acid to polyimide, the electrode was then treated in a tube furnace using the same curing procedure as described in Example 1.

Example 6

10 Coin cell preparation, Capacity and Rate Performance of PI Coated LTO Electrode and Comparative Electrodes

Using the prepared electrodes from example 5 and comparative examples A and B, electrode disks, 13 mm OD, were cut with a punch
15 (HSNG-EP, Hohsen Corp.), and dried for 10 hours under vacuum at 120 °C. Separator disks, 16.8 mm OD, were cut with a punch and dried in the antechamber of a glove box for 10 hours, under vacuum, at room temperature. Lithium foil disks, 15 mm OD, were cut with a punch (Elora, Germany) in an argon-filled glove box. Coin cells (size CR2320 using cell
20 parts from Hohsen Corp) were assembled in a glove box under an argon purge using the electrode disk as the cathode, the lithium disk as the anode, the separator disk disposed between the anode and cathode disks, and 1.0M LiPF₆ in EC/EMC (30/70 volume basis) as electrolyte. The coin cells were finished by sealing with an auto crimper (Hohsen Corp.). Using
25 this method, coin cells were prepared from 1 % PI coated LTO ("1 % PI coat"), 2 % PI coated LTO ("2 % PI coat") and 3 % PI coated LTO ("3 % PI coat") from example 4; uncoated LTO ("0 % PI Coat") from comparative A; and, polyimide binder ("PI binder") from comparative B.

The coin cells thus prepared (electrode/Li half cells) were tested in
30 a battery charger (Maccor, USA) by the following test protocol: a) rest 24 hours; b) five discharge-charge cycles in the range of 1.0 to 2.5 V for each cycle rate of 0.1C, 1C, 5C and 10C. The cycle rate "C" is the number of complete charges and discharges per hour. Thus a rate of 10C means 5 charges and 5 discharges per hour, or in other words, 6 minutes to
35 completely charge or discharge the cell.

The coin cell test results are summarized in Table 1. The data, shown as capacity (mAh/g), is an average of the five discharge-charge

- 5 cycles at each cycle rate. In this set of tests, the capacity performance of 1 % PI coating is undiminished compared to the uncoated LTO. The 2 % and 3 % PI coating and the PI binder show capacity loss at all cycle rates tested.

Table 1

Cycle Rate	Capacity (mAh/g)				
	0 % PI coat	1 % PI coat	2 % PI coat	3 % PI coat	PI binder
0.1C	170	170	159	156	163
1C	162	162	146	138	157
5C	119	122	103	88	101
10C	90	90	71	60	70

10

Example 7

Cylindrical Large Cell with 1 % PI Coated LTO Anode

- To determine the effect of polyimide coating on gas generation in LTO batteries, a cylindrical large cell (nominal 1000 mAh) equipped with pressure monitor was designed and used. Lithium iron phosphate (LFP) cathode was used as counter electrode, due to its excellent stability and non-gassing feature.

- For the anode, 1 % polyimide coated LTO from Example 1 (12.6720 g) and conductive carbon (1.5840 g) were mixed evenly in 4 glass vials (20 mL size) by a Spex mixer for 30 minutes before adding NMP (26.3594 g) and PVDF solution (12.1846 g, 13 % in NMP) to form the anode paste with a solid content of 30 wt % and a ratio of carbon:PVDF:LTO (10:10:80).

- For the cathode, LFP material (16.0 g) and conductive carbon (2.0 g) were mixed evenly in 4 glass vials (20 mL size) by a Spex mixer for 30 minutes before adding NMP (40.693 g) and PVDF solution (15.3858 g) to form the cathode paste with a solid content of 27 wt % and a ratio of carbon:PVDF:LFP (10:10:80).

5 Glass beads (6 pieces for each vial, diameter 4 mm) were added to each of the pastes which were then thoroughly mixed in the Spex mixer for 1 hour, stopping periodically (every 15 minutes) to prevent the paste from getting too warm.

The electrodes were prepared from the pastes as follows. A clean glass plate (27 cm by 19 cm) was placed on the top of vacuum plate (30 cm by 23 cm). A piece of copper foil was placed on the glass plate. The anode or cathode paste was spread on the foil with a doctor-blade at a constant speed using the gate of 10 mils (0.250 mm) to form a film and the film was dried at 120 °C under nitrogen flow for 30 minutes. The film was further dried at 120 °C under vacuum for 10 hours and then allowed to cool to room temperature under vacuum. The prepared electrodes were pressed by a calendar machine (Design Prove Machine, Canada) under about 590 psi (4068 kPa) as described in example 5. The electrodes were cut into a size of 20 cm by 5 cm with a taper of 2 cm by 3 cm on the edge for cell assembly. The areal density of active material LTO on the electrode is about 6.0 mg/cm²; the areal density of LFP is about 6.5 mg/cm².

The full cell was made by stacking separator-anode-separator-cathode for four times to get a total active electrode area of 800 cm², and then rolled into the cylindrical cell. Electrolyte (30 g, 1M LiPF₆ in EC/EMC (30/70)) was added to completely wet the electrode. The cell was sealed and attached with a pressure sensor to monitor pressure change and a vessel to sample gases for analysis.

30 Example 8

Cylindrical Large Cell with 2 % PI coated LTO Anode

Using the method of Example 7 and the polyimide coated LTO from Example 2, a cylindrical large cell was prepared with 2% polyimide coated LTO as the anode.

5

Comparative Example C
Cylindrical Large Cell with Graphite Anode

In order to compare gas generation from graphite based batteries, a graphite/LFP cylindrical large cell was made according to the method of Example 6 using an ingredients weight ratio of graphite:carbon black:PVDF equal to 88:2:10. The active material areal density was 6.05 mg/cm². To match the capacity of this anode, a LFP electrode was made with an areal density of 12.5 mg/cm².

15

Comparative Example D
Cylindrical Large Cell with Uncoated LTO Anode

Using the method of Example 7 and uncoated LTO in place of the coated LTO, a cylindrical large cell was prepared with uncoated LTO as the anode.

20

Comparative Example E
Cylindrical Large Cell with Uncoated LTO and Polyimide Binder

A cylindrical large cell was prepared using the method of Example 7 except the uncoated LTO electrode with polyimide binder from Examples B was used as the anode.

25

30

Example 9
Testing of Cylindrical Large Cells

The cylindrical large cells were tested by the following procedures: open circuit voltage rest 12 hours; formation at 0.2C, 3 cycles; rest 10 hours; cycling at 1C, for 115 hours. During the electrochemical test, the gas generation was monitored by a pressure sensor equipped with the cell. The gas volume produced was calculated from the pressure rise assuming ideal gas behavior. Results are summarized in Table 2.

35

- 5 Uncoated LTO in Comparative D generated a substantial amount of gas (1.27 mL per gram of electro-active material) at 100 hours compared to a typical commercial-type graphite anode (0.52 mL/g) of Comparative C. The 1 % PI coating in Example 6 reduced gas generation of LTO anode to 0.52 mL/g, a level equal to graphite. At the higher 2 % PI coating, gas
- 10 generation was reduced even further (to 0.39 mL/g), although the capacity is also decreased.

Table 2

	Comp. C graphite	Comp. D no PI	Ex. 6 1 % PI	Ex. 7 2 % PI	Comp. E PI binder
Weight (g) of Active material	2.13	6.40	4.85	4.37	4.37
Capacity (mAh), (theoretical)	792	1114	844	760	760
Capacity (mAh) at 0.2C	450	605	610	510	600
Capacity (mAh) at 1C	410	460	490	430	510
Pressure (kPa) at 100 hours	24.1	104.7	40.7	31.0	25.5
Gas, mL/g active	0.52	1.27	0.52	0.39	0.28

15

Example 10

Al₂O₃-modified LTO Coated with Polyimide

- Lithium titanate modified with Al₂O₃ was prepared as follows. Sodium aluminate (615 mg) was dissolved in 160 mL of DI water and
- 20 stirred to dissolve completely. Boric acid (439 mg) and citric acid (56 mg) were dissolved separately in 160 mL of DI water. Lithium titanate (25 g) was suspended in 250 mL of DI water and the temperature of the suspension was adjusted to 45 °C. The solutions of sodium aluminate and boric and citric acid are added simultaneously and at equal rates,

5 approximately 8 mL/min, while stirring. The solution was stirred for an additional 30 minutes after the addition is complete, after which the particles were separated from the liquid by vacuum filtration. The recovered particles were washed with deionized water, dried in a vacuum oven at 120 °C for 2 hr, and annealed in an oven for 5 hr at a temperature
10 of 450 °C. The treatment of LTO creates alumina on the surface of the LTO particles which are referred to as Al₂O₃-modified LTO.

The Al₂O₃-modified LTO was then coated with polyimide (1 wt % PI) as described in Example 1.

The rate performance of Al₂O₃-modified LTO before and after
15 polyimide was tested following the same procedure as Example 6. The gassing behavior of Al₂O₃-modified LTO before and after polyimide was measured following the same procedure as Example 7 and 9. The testing results are summarized in Table 3. The polyimide coating effectively reduced gassing of Al₂O₃-modified LTO material.

20

Example 11

MnO_x-modified LTO Coated with Polyimide

MnO_x-modified LTO was prepared as follows. LTO, 34.648 g, and
25 deionized water, 200 mL, were placed in a 500 mL three neck round bottom flask. The slurry was agitated at 350 rpm by overhead stirrer. KMnO₄(aq) (0.4M, 8.2 mL), was added to the slurry and the slurry was heated to about 60 °C. Sucrose, 6 g, was added in the slurry which was kept at temperature for about 10 min under the agitation. The slurry was
30 filtered to collect the powders. The powders, washed with deionized water, were dried under vacuum at room temperature and then further dried in an oven at 120 °C for 2h under vacuum. Finally, the dried powders were heated at 300 °C for 1h in air. The heating and cooling rates were set to 5 °C per min. "MnO_x" refers to a mixture of manganese oxide species. The
35 Mn valence state was predominately 4+ and MnO_x was predominately MnO₂. The MnO_x-modified LTO thus prepared had an approximately 0.74 wt % MnO₂ coating based on the total weight of MnO_x-modified LTO.

5 The MnO_x-modified LTO was then coated with polyimide (1 wt % PI) as described in Example 1.

 The rate performance of MnO_x-modified LTO before and after polyimide coating was tested following the same procedure as Example 6. The gassing behavior of MnO_x-modified LTO before and after polyimide
10 was measured following the same procedure as Example 7 and 9. The test results are summarized in Table 3. The polyimide coating reduced gassing of MnO_x-modified LTO material.

Table 3

Example	Rate performance		Gassing rate (ml/min)	
	0.1C (mAh/g)	5C (mAh/g)	Formation	Cycling
10 Al ₂ O ₃ -LTO	169	159	0.43	0.89
10 PI-coated Al ₂ O ₃ -LTO	162	145	0.13	0.31
11 MnO _x -LTO	169	158	0.71	1.38
11 PI-coated MnO _x -LTO	167	147	0.54	1.08

15

Example 12

LTO Coated with BPDA-PPD Polyimide

 Poly(amic acid) precursor solution was prepared from poly(p-phenylene biphenylenetetracarboximide) (BPDA-PPD) and coated on LTO
20 following the procedure of Example 1. The rate performance of this BPDA-PPD coated LTO was tested following the same procedure as Example 6. The results are summarized in Table 4. Gassing tests were not run.

Example 13

25

LTO Coated with Phenolic-containing Fluorinated Polyimide

 LTO was coated with an alcohol-soluble phenolic-containing fluorinated polyimide. The coating process was based on the procedure of Example 1 except that curing step was omitted as the coating is already

- 5 imidized. After depositing the polymer onto LTO, the coated material was achieved by drying in vacuum oven for 10 hours at 120 °C and 2 hours at 150 °C. The rate performance of this PI-coated LTO material was tested following the same procedure as Example 6. The gassing behavior of this PI-coated LTO material was measured following the same procedure as
- 10 Example 7 and 9. The results are summarized in Table 4.

Table 4

Example	Rate performance		Gassing rate (ml/min)	
	0.1C (mAh/g)	5C (mAh/g)	Formation	Cycling
12	166	112	----	----
13	164	108	0.23	----

5

CLAIMS

What is claimed is:

1. A coated particle comprising a lithium titanate particle core encased
10 by a polyimide coating, wherein the weight percent of polyimide coating is
in the range of 0.1% to 5% based on the total weight of coated particle.
2. The coated particle of claim 1 wherein the weight percent of
polyimide coating is in the range of 0.2% to 3% based on the total weight
15 of coated particle.
3. The coated particle of claim 1 wherein the weight percent of
polyimide coating is in the range of 0.3% to 2.0% based on the total weight
of coated particle
20
4. A plurality of coated particles according to any one of claims 1, 2 or
3 wherein said plurality of particles has a volume median particle size in
the range of 0.1 μm to 100 μm .
- 25 5. The coated particle of claim 1 wherein the polyimide is comprised of
monomers pyromellitic dianhydride and oxydianiline.
6. An electrode comprising a plurality of coated LTO particles
according claim 1 as an electro-active material.
30
7. The electrode of claim 6 further comprising any one or combination
of components selected from the group consisting of binder and
conductivity agent.
- 35 8. A lithium ion battery comprising an anode, a cathode, a separator
and electrolyte wherein said anode is the electrode of claim 6 or 7.

- 5 9. A lithium ion battery comprising an anode, a cathode, a separator
and electrolyte wherein said anode comprises a plurality of coated LTO
particles according to claim 4.

10

1/5



FIG. 1A



FIG. 1B

2/5

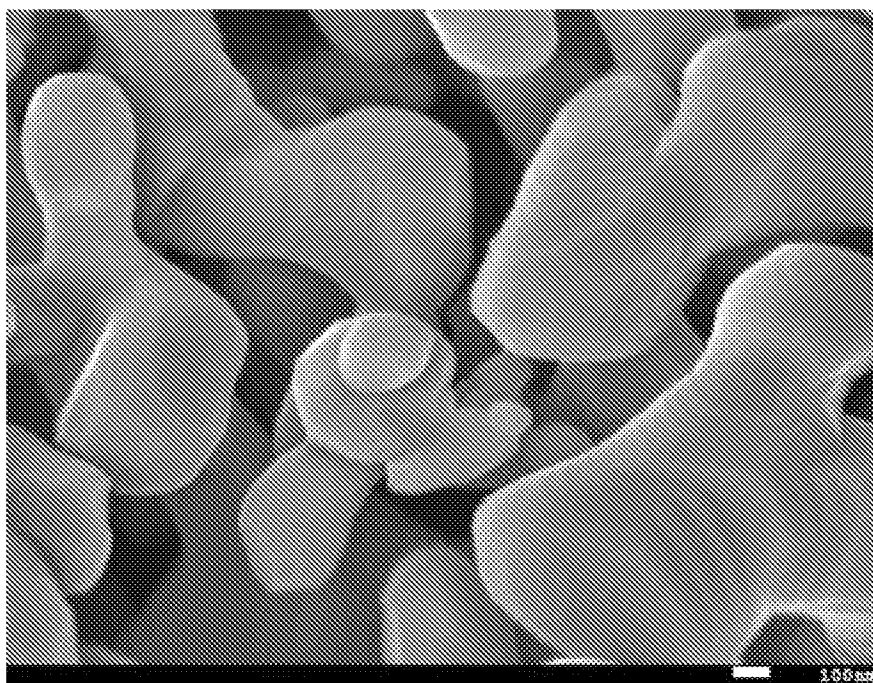


FIG. 2A

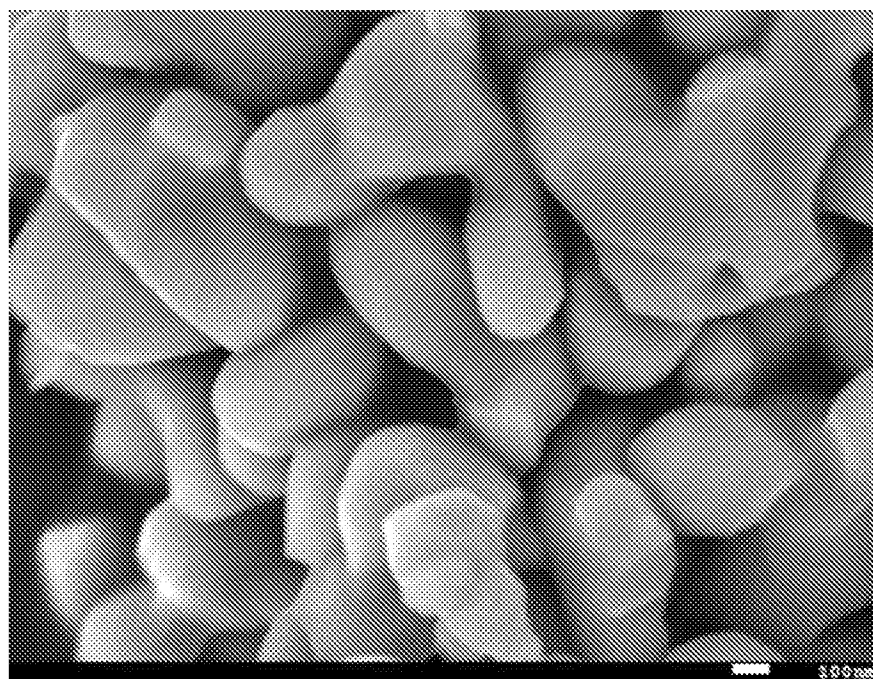


FIG. 2B

3/5

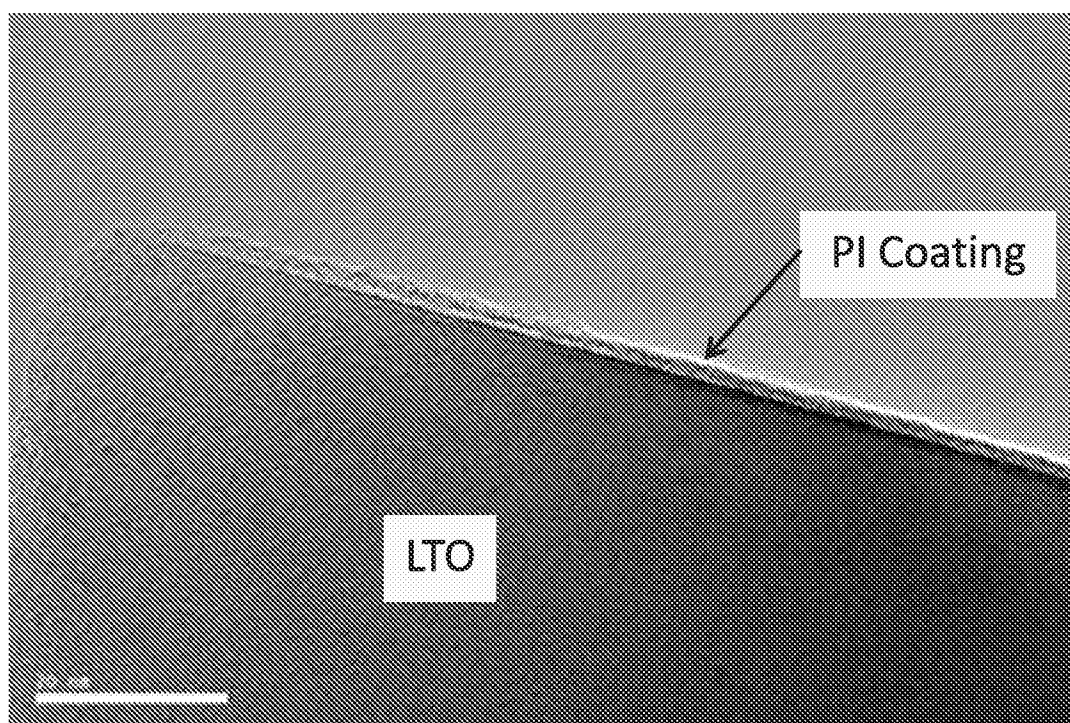


FIG. 3

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ATR Scans

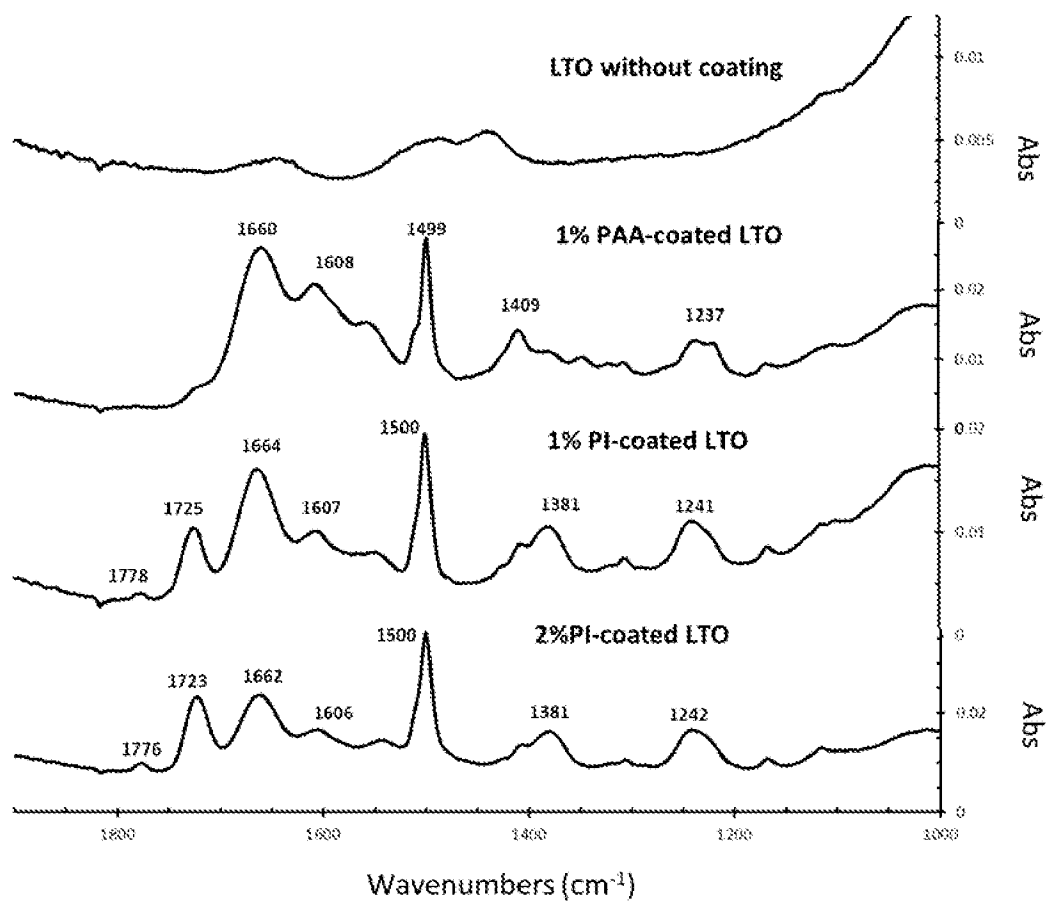


FIG. 4

5/5

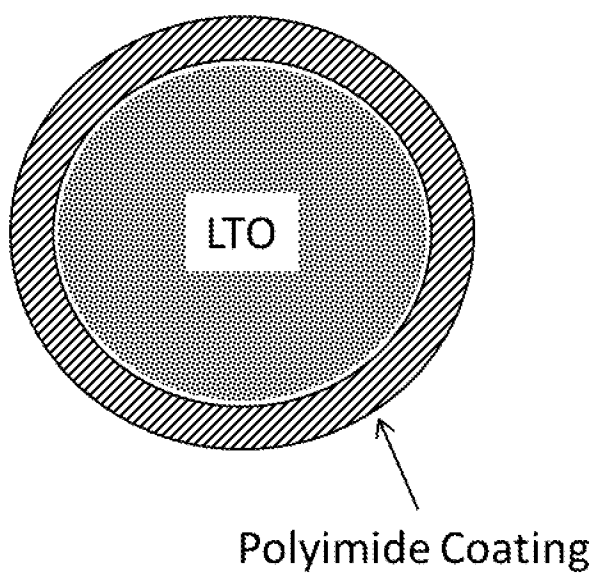


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/068762

A. CLASSIFICATION OF SUBJECT MATTER INV. C01G23/00 C09C1/36 H01M4/00 H01M4/36 H01M4/485 ADD.		
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) C01G C09C H01M		
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, CHEM ABS Data, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2012/111546 A1 (TOSHIBA KK [JP]; YAMAMOTO DAI [JP]; IWASAKI TAKUYA [JP]; HARADA YASUHI) 23 August 2012 (2012-08-23) paragraphs [0001] - [0154] -----	1-9
A,P	EP 2 677 574 A1 (TOSHIBA KK [JP]) 25 December 2013 (2013-12-25) paragraphs [0002], [0008] - [0027], [0044] - [0067], [0129] - [0157] ----- -/--	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 12 February 2015		Date of mailing of the international search report 26/02/2015
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 Corrias, M

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/068762

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	YAN-BING HE ET AL: "Carbon coating to suppress the reduction decomposition of electrolyte on the LiTiO₂ electrode", JOURNAL OF POWER SOURCES, ELSEVIER SA, CH, vol. 202, 15 November 2011 (2011-11-15), pages 253-261, XP028440059, ISSN: 0378-7753, DOI: 10.1016/J.JPOWSOUR.2011.11.037 [retrieved on 2011-12-09] "Introduction", "Experimental", "Results and discussion" -----	1-9
A	US 2012/244439 A1 (YU YONG-MI [KR] ET AL) 27 September 2012 (2012-09-27) paragraphs [0019] - [0059] -----	1-9
A	US 2013/260020 A1 (TOMIKAWA MASAO [JP] ET AL) 3 October 2013 (2013-10-03) paragraphs [0010] - [0054] -----	1-9
A	US 2013/273254 A1 (HSU YEN-HUEY [TW] ET AL) 17 October 2013 (2013-10-17) paragraphs [0026] - [0043] -----	1-9
A,P	QINGWEN LU ET AL: "A polyimide ion-conductive protection layer to suppress side reactions on Li₄Ti₅O₁₂ electrodes at elevated temperature", RSC ADVANCES, vol. 4, no. 20, 11 February 2014 (2014-02-11), page 10280, XP55169219, ISSN: 2046-2069, DOI: 10.1039/c3ra47694d the whole document -----	1-9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2014/068762

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2012111546 A1	23-08-2012	CN 103210531 A EP 2677574 A1 JP 2012174350 A US 2013337315 A1 WO 2012111546 A1	17-07-2013 25-12-2013 10-09-2012 19-12-2013 23-08-2012
EP 2677574 A1	25-12-2013	CN 103210531 A EP 2677574 A1 JP 2012174350 A US 2013337315 A1 WO 2012111546 A1	17-07-2013 25-12-2013 10-09-2012 19-12-2013 23-08-2012
US 2012244439 A1	27-09-2012	KR 20120108746 A US 2012244439 A1	05-10-2012 27-09-2012
US 2013260020 A1	03-10-2013	CN 103238241 A JP 5338924 B2 KR 20130079638 A SG 190422 A1 TW 201242148 A US 2013260020 A1 WO 2012073853 A1	07-08-2013 13-11-2013 10-07-2013 31-07-2013 16-10-2012 03-10-2013 07-06-2012
US 2013273254 A1	17-10-2013	JP 2013221150 A TW 201341436 A US 2013273254 A1	28-10-2013 16-10-2013 17-10-2013