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(54) Title: METAL-CONTAINING COMPOUNDS

(57) Abstract: The invention relates to a novel solid state process for the preparation of an alkali metal (metal)-containing compound comprising i) forming a mixture comprising two or more precursor compounds, at least one of which comprises at least one alkali metal, and ii) heating the mixture comprising the two or more precursor compounds under an atmosphere consisting of one or more organic compounds in gaseous form and optionally nitrogen and/or one or more inert gases, wherein the one or more organic compounds in gaseous form are selected from aliphatic alcohols, aldehydes, carboxylic acids, ketones, glyoxylic acid, dimethyl aminoborane and trimethyl aminoborane. Materials made by such a process are useful, for example, as electrode materials in alkali metal-ion battery applications.

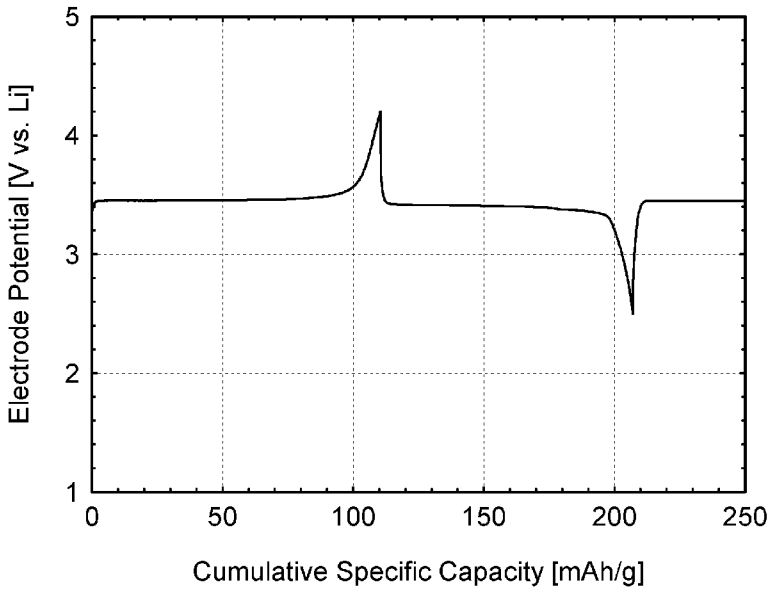

FIGURE 1A

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METAL-CONTAINING COMPOUNDS

FIELD OF THE INVENTION

The present invention relates to a novel process for the preparation of alkali metal (metal)-containing compounds.

BACKGROUND OF THE INVENTION

Lithium-ion battery technology has enjoyed a lot of attention in recent years and provides the preferred portable battery for most electronic devices in use today. Such batteries are "secondary" or rechargeable which means they are capable of undergoing multiple charge/discharge cycles. Typically lithium-ion batteries are prepared using one or more lithium electrochemical cells containing electrochemically active materials. Such cells comprise an anode (negative electrode), a cathode (positive electrode) and an electrolyte material. When a lithium-ion battery is charging, Li^+ ions de-intercalate from the cathode and insert into the anode. Meanwhile charge balancing electrons pass from the cathode through the external circuit containing the charger and into the anode of the battery. During discharge the same process occurs but in the opposite direction.

Various electrochemically active materials have been suggested for use as the cathode materials, for example $LiCoO_2$, $LiMn_2O_4$ and $LiNiO_2$, see US 5,135,732 and US 4,246,253. However these materials exhibit problems, for example cycle fading (depletion in charge capacity over repeated charge/discharge cycles), which make them commercially unattractive. Attempts to address cycle fading have led to lithium metal phosphate and lithium metal fluorophosphates becoming favourable materials. Such materials were first reported in US 6,203,946, US 6,387,568, and by Goodenough et al. in "Phospho-olivines as Positive-Electrode Materials for Rechargeable Lithium Batteries", Journal of Electrochemical Society, (1997) No. 144, pp1188-1194.

Many workers have tried to provide economical and reproducible synthesis methods for phosphate-containing materials, and especially for high performance (optimised) phosphate-containing materials. A review of the prior art methods which describe the preparation of one particular lithium metal phosphate, namely, lithium iron phosphate ($LiFePO_4$), is given by X. Zhang et al in "Fabrication and Electrochemical Characteristics of $LiFePO_4$ Powders for Lithium-Ion Batteries", KONA Powder and Particle Journal No. 28 (2010) pp 50-73. As this review demonstrates, a lot of effort has been expended since lithium iron phosphate was first identified in 1997, to find the most expedient method for producing a $LiFePO_4$ material with the best all round performance; for example solid-state

synthesis using mechanochemical activation to increase the activation of the starting materials, microwave heating to control the particle size of the active cathode material, and carbothermal reduction which enables Fe(III) e.g. in the form of Fe_2O_3 or $FePO_4$ (i.e. cheap and readily available sources of iron) to be used as a precursor material. The carbothermal reduction process is a high-temperature reduction reaction (typically 550°C to 850°C) which commonly utilizes carbon black, graphite or pyrolyzed organic chemicals as the source of carbon reducing agent. Carbothermal reduction is a highly endothermic reaction, hence the reaction temperature must be sufficient to drive the reaction. In addition, since solid carbon is used as the reducing agent, all the precursors and reactants must be kept in good contact throughout the reaction, nevertheless as reported in the review mentioned above, carbothermal reduction is excellent for the reduction of Fe(III), the stabilization of Fe(II), the control of particle morphology, and the enhancement of electrical conductivity by coating $LiFePO_4$ with residual carbon.

Particulate reducing agents other than carbon, specifically silicon oxide, titanium oxide and elemental metals such as Fe, Co, Ni, Mn, Cu, V, Ti, Cr, Nb, Mo, Mg, Ca, Zn, Sr, Pb, Cd, Sn, Ba, Be, Al and B are disclosed in EP1 343 720.

The most interesting cathode materials are those which have large charge capacity, are capable of good cycling performance, highly stable, and of low toxicity and high purity. To be commercially successful, the cathode materials must also be easily and affordably produced. This long list of requirements is difficult to fulfil but, as detailed in the review mentioned above, the active materials most likely to succeed are those with small particle size and narrow size distribution, with an optimum degree of crystallinity, a high specific surface area and with uniform morphology.

Materials containing hypophosphite ions ($H_2PO_2^-$), such as sodium hypophosphite (NaH_2PO_2) and ammonium hyphophosphite ($NH_4H_2PO_2$) are available very cheaply and widely used as the in-situ reducing agent for electroless plating baths; they reduce metal salts (e.g. nickel salts) to elemental metal (e.g. Ni) in the plating process. Dimethylamine borane (DMAB), trimethylamine borane, and borohydride materials are used for similar applications and formaldehyde is also known to reduce copper salt containing solutions to copper metal. Other reducing agents include: materials containing hydrosulfite ions, such as sodium hydrosulfite ($Na_2S_2O_4$) (also referred to as sodium hyposulfite and sodium dithionite), sodium sulfite (Na_2SO_3), and hydrazine; all are used to reduce organic compounds.

Yang et al. disclose in *J Power Sources* 179, 357, 2008 that MoO_2 can be synthesized by reducing MoO_3 using ethanol vapour at 400^{0}C. Patent document EP 2004548, teaches a process for producing nanostructured olivine lithium metal phosphate ($LiMPO_4$) particles characterized by the use of a polyol method which includes the precipitation of a solid while heating sufficient precursors in a solvent comprising a multivalent alcohol with a high-boiling point for example glycols with the general formula HO-(-C_2H_4O-).sub.n-H where n=1-10 or HO-(-C_3H_6O-).sub.n.-H where n= 1-10, or other polyols with the general formula $HOCH_2$-(-C_3H_5OH-).sub.n-H where n=1-10, like for example the tridecane- 1,4,7, 10,13 –pentanol. This latter process has certain disadvantages however, in that the high boiling point multivalent alcohol solvent must be removed from the reaction product before it is able to be used and this creates an expensive multistep process.

A number of prior art documents, for example EP2624344A, WO2003/038930A, CN102942167A, EP2309573A and EP1261050A, describe the preparation of transition metal phosphate-containing materials using one or more gaseous reducing agents such as hydrogen gas, ammonia, and carbon monoxide. Further documents, including US2006/0091362A, US2006/0093919A and WO2008/033717A, disclose a similar reaction that uses a hydrocarbon-containing reducing atmosphere (specifically methane) which is created by carbonizing the hydrocarbon during the heating step to form a reducing carbon material. Finally, US2007/0134554A describes a method of synthesizing a compound of the formula $Li_xM_{1-y}M'_y(XO_4)_n$, involving reacting precursor compounds in a reducing gaseous atmosphere comprising one or more of carbon monoxide, hydrogen gas and ammonia. Such a reducing atmosphere is preferably produced by the decomposition in a vacuum or an inert atmosphere of an organic compound. Polyethylene, polypropylene, glucose, fructose, sucrose, xylose, sorbose, starch, cellulose, esters of cellulose, block polymers of ethylene and ethylene oxide and polymers of furfuryl alcohol are organic compounds which are specifically disclosed in this document.

The present invention aims to provide an alternative, fast, reliable and cost effective process for the preparation of alkali metal (metal)-containing compounds. Advantageously, the process of the present invention aims to provide alkali metal (metal)-containing compounds that meet the structural and alkali ion insertion properties needed for commercially viable cathode active materials.

To this end, the present invention provides a solid state process for the preparation of an alkali metal (metal)-containing compound comprising i) forming a mixture comprising two

or more precursor compounds, at least one of which comprises at least one alkali metal, and ii) heating the mixture comprising the two or more precursor compounds under an atmosphere consisting of one or more organic compounds in gaseous form and optionally nitrogen and/or one or more inert gases, wherein the one or more organic compounds in gaseous form are selected from aliphatic alcohols, aldehydes, carboxylic acids, ketones, glyoxylic acid, dimethyl aminoborane and trimethyl aminoborane.

The most preferred one or more organic compounds in gaseous form are selected from aliphatic alcohols (for example ethanol, isopropanol), aromatic alcohols (for example phenyl ethanol and benzyl alcohol), aldehydes (for example formaldehyde), and acids or acid salts (for example glyoxylic acid and formic acid).

In a preferred process of the present invention, at least one of the precursor compounds in the mixture comprises one or more metals selected from transition metals, non-transition metals and metalloids. In the context of this invention, the term “metalloid” is an element with both metal and non-metal characteristics.

The term “precursor compound” as used herein, is defined as a compound that contributes one or more elements to the target alkali metal (metal)-containing compound. Ideally, prior to the reaction with one or more organic compounds in gaseous form, the mixture of the two of more precursor compounds is substantially free of any other compound which is not a precursor material. In particular, the mixture of two or more precursor compounds is preferably substantially free of any solvent, for example one or more organic solvents, inorganic solvents or water, and preferably the two or more precursor compounds are in solid state form. Further ideally, in the process of the present invention at least one of the precursor compounds comprises one or more transition metals and at least one of which is reduced by the one or more organic compounds in gaseous form.

The one or more organic compounds used in the present invention are liquids or solids at standard temperature and pressure. The process of the present invention preferably involves heating the mixture of two or more precursor compounds at a temperature below that which the one or more organic compounds undergo pyrolysis. “Pyrolysis” as used herein is defined as the process of thermal decomposition of the organic compounds to materials such as carbon, carbon monoxide, hydrogen gas and ammonia. The reaction mechanism by which the present invention preferably proceeds is other than one that involves the breaking up of the one or more organic compositions into carbon, carbon

monoxide, hydrogen gas or ammonia. The gaseous form of the one or more organic compounds may generated prior to contact with the mixture of two or more precursor compounds, i.e. the one or more organic compounds in liquid or solid form are not in contact with the two or more precursor compounds during the present invention. For example, the atmosphere consisting of the one or more organic compounds in gaseous form may be generated by heating a source of the one or more organic compounds to cause them to enter the gaseous phase. The resulting one or more organic compounds in gaseous form are then directed into a reaction vessel containing a mixture of two or more precursor compounds. A flow of nitrogen and/or one or more inert gases may be used to assist in carrying and directing the one or more organic compounds in gaseous form into the reaction vessel.

Alternatively an atmosphere containing one or more organic compounds in gaseous form, may be generated by bubbling a stream of nitrogen and/or one or more inert gases through a source of one or more organic compounds and then directing the resulting mixture of inert gas entrained by one or more organic compounds into a reaction vessel containing the mixture of two or more precursor compounds.

Further alternatively, one or more of the organic compounds may be passed through a nebuliser or injected directly into a heated furnace that contains the mixture of two or more precursor compounds.

Advantageously, the present invention involves a simple and single-step process without the need for the removal of excess or un-reacted organic compound.

In a highly preferred process of the present invention at least one of the two or more precursor compounds comprises one or more alkali metals and optionally this precursor compound may also comprise one or more metals selected from transition metals and/or non transition metals and/or metalloids. Additional separate transition metal- and/or non transition metal- and/or metalloid-containing precursor compound(s) may also be used, especially, but not exclusively, when the alkali metal-containing precursor compound does not already comprise a transition metal, non transition metal and/or metalloid.

A preferred solid state process of the present invention produces an alkali metal (metal)-containing compound of the formula:

$A_aM_b(X_cY_d)_eZ_f$

wherein:

A is an alkali metal selected from one or more of lithium, sodium and potassium;

M comprises one or more metals selected from transition metals, non-transition metals and metalloids;

$(X_cY_d)_e$ is at least one first anion; and

Z is at least one second anion

wherein a > 0; b >0; c > 0; d ≥ 0; e > 0 and f ≥ 0;

wherein a, b, c, d, e and f are chosen to maintain electroneutrality.

Desirably, the process of the present invention produces an alkali metal (metal)-containing compound, for example of the formula $A_aM_b(X_cY_d)_eZ_f$, in which M comprises one or more transition metals and/or non transition metals and/or metalloids which have an average oxidation state which is lower than the average oxidation state of the one or more metals (transition metals and/or non transition metals and/or metalloids) in the precursor compounds.

In particularly preferred alkali metal (metal)-containing compounds according to the present invention:

M comprises one or more metals selected from transition metals such as titanium, vanadium, niobium, tantalum, hafnium, chromium, molybdenum, tungsten, manganese, iron, osmium, cobalt, nickel, palladium, platinum, copper, silver, gold, zinc, cadmium, scandium, yttrium, zirconium, technetium, rhenium, ruthenium, rhodium, iridium, mercury and bismuth, non transition metals such as aluminium, gallium, indium, tin, lead, magnesium, calcium, beryllium, strontium and barium, and metalloids such as boron, silicon, germanium, arsenic, antimony, selenium and tellurium;

X comprises one or more elements selected from titanium, vanadium, chromium, arsenic, molybdenum, tungsten, niobium, manganese, aluminium, selenium, boron, oxygen, carbon, silicon, phosphorus, nitrogen, sulfur, fluorine, chlorine, bromine and iodine.

Y comprises one or more halides, sulfur-containing groups, oxygen-containing groups and mixtures thereof;

Z is selected from one or more halides, hydroxide-containing groups and mixtures thereof.

Desirable compounds of the formula $A_aM_b(X_cO_d)_eZ_f$ include, but are not limited to, those in which A is lithium and/or sodium, and in which the first anion $(X_cY_d)_e$ comprises one or

more groups, preferably selected from phosphate, condensed polyphosphate, phosphide, sulfate, sulfide, oxide, thiosulfate, sulfite, chlorate, bromate, oxyhalide, halide, silicate, arsenate, selenate, molybdate, vanadate groups and any oxyanion groups. Compounds where X comprises phosphorus, for example in which $(X_cY_d)_e$ is a PO_4 and/or P_2O_7 moiety are especially preferred. Similarly, compounds in which X comprises sulfur are equally advantageous, such as those containing SO_4 moieties.

Other favourable materials include:

$LiFePO_4$,

$LiFePO_4/Fe_2P$,

$LiMnPO_4$,

$LiCoPO_4$,

$LiNiPO_4$,

$NaFePO_4$,

$NaMnPO_4$,

$NaCoPO_4$,

$NaNiPO_4$,

$LiMn_{0.5}Fe_{0.2}Mg_{0.3}PO_4$,

$Li_3V_2(PO_4)_3$,

$Na_4Fe_3(PO_4)_2P_2O_7$,

$Na_3V_2(PO_4)_3$,

Na_xMnO2

$LiMn_{0.5}Fe_{0.5}PO_4$,

$Na_7V_4(P_2O_7)_4PO_4$,

$Na_7V_3(P_2O_7)_4$,

$Na_2Fe(SO_4)_2$,

$NaVPO_4F$,

$LiVPO_4F$,

$Na_3V(PO_4)_2$,

$Li_3V(PO_4)_2$,

$NaVOPO_4$,

$LiVOPO_4$,

LiV_2O_5,

NaV_2O_5,

$NaVO_2$,

$Na_{8-2x}Fe_{4+x}(P_2O_7)_4$,

$Na_{8-2x}Mn_{4+x}(P_2O_7)_4$,

$Na_2MnP_2O_7$,
$Na_2FeP_2O_7$,
$Na_2CoP_2O_7$,
$Na_4Mn_3(PO_4)_2P_2O_7$,
$Na_4Co_3(PO_4)_2P_2O_7$,
$Na_4Ni_3(PO_4)_2P_2O_7$,
$NaFeSO_4F$,
$LiFeSO_4F$,
$NaMnSO_4F$,
$LiMnSO_4F$,
Na_2FePO_4F,
Na_2MnPO_4F,
Na_2CoPO_4F,
Na_2NiPO_4F,
$Na_2Fe_2(SO_4)_3$,
$Li_2Fe_2(SO_4)_3$, and
$Li_2Fe(SO_4)_2$.

In particular, the present invention provides a solid state process for the preparation of a compound comprising a lithium metal phosphate of the general formula: $LiMPO_4$, where M comprises a metal selected from one or more of manganese, iron, cobalt, copper, zinc, nickel, magnesium and calcium, the process comprising i) forming a mixture of two or more precursor compounds and ii) heating the mixture of precursor compounds under an atmosphere consisting of one or more organic compounds in gaseous form and optionally nitrogen and/or one or more inert gases, wherein the one or more organic compounds in gaseous form are selected from aliphatic alcohols, aldehydes, carboxylic acids, ketones, glyoxylic acid, dimethyl aminoborane and trimethyl aminoborane.

Preferred $LiMPO_4$–containing compounds include $LiFePO_4$-containing compounds and these may be produced in the process of the present invention by i) forming a mixture of two or more precursor compounds wherein one or more of the precursor compounds are selected from LiH_2PO_4, Li_2HPO_4, LiOH, $LiOH.H_2O$, Fe_3O_4, Fe_2O_3, Li_2CO_3, $FePO_4.xH_2O$, $FePO_4$, $Fe_3(PO_4)_2$, $FeSO_4.xH_2O$, $Fe(NO_3)_3.xH_2O$, $Fe(CH_3CO_2)_2$, $C_6H_8O_7$ $.xFe^{3+}.yNH_3$ (ammonium iron (III) citrate), $C_6H_5FeO_7$ (iron (III) citrate) and $Fe(C_5H_7O_2)_3$ (iron (III) 2,4-petanedionate), $Fe(C_2O_4).2H_2O$, P_2O_5, H_3PO_4, and ii) heating the mixture of precursor compounds under an atmosphere consisting of one or more organic compounds in

gaseous form and optionally nitrogen and/or one or more inert gases, wherein the one or more organic compounds in gaseous form are selected from aliphatic alcohols, aldehydes, carboxylic acids, ketones, glyoxylic acid, dimethyl aminoborane and trimethyl aminoborane.

Ideally the two or more precursor compounds are intimately admixed in particulate form. This can be achieved using various methods, for example by finely grinding the materials separately using a pestle and mortar or a ball mill, and then mixing them together, or the materials can be admixed whilst they are being finely ground. The grinding and admixing is of sufficient duration to produce a uniformly intermixed finely ground powder. A solvent such as acetone or another material which is easily removed, for example a low boiling liquid can be used to assist the grinding/admixing process and this is removed prior to the reaction with the one or more organic compounds in gaseous form. Other known techniques such as high energy ball milling and microwave activation may also be used to help prepare the starting materials, for example to increase their reactivity. It might be expected that the reaction would be facilitated by an increase in the surface area of the precursor compounds. However, surprisingly, it has been found that pressing the precursor compounds into pellets, preferably after grinding as described above, can yield a final target material with a higher level of phase purity than using the mixture of ground precursor compounds in non-pelleted form.

The reaction between the two or more precursor compounds typically occurs during the heating step of the process and in the presence of the one or more organic compounds in gaseous form. The heating step typically involves heating the mixture of precursor compounds either at a single temperature, or over a range of temperatures, for example up to at least 200°C, preferably up to at least 400°C. A single or a range of reaction temperatures of from 150°C to 1200 °C is preferred with from 150°C to 800°C being particularly preferred. The reaction is preferably conducted in a furnace. The reaction temperature of the process is ideally below the temperature at which the one or more organic compounds undergo pyrolysis and this will be dependent on the particular organic compounds and precursor compounds being used.

Conveniently the solid state process of the present invention is performed by placing the two or more precursor compounds in a ceramic boat which is put in a quartz tube or similar, and heated using a furnace. The tube containing the ceramic boat may be sealed under an atmosphere consisting of the one or more organic compounds in gaseous form and optionally nitrogen and/or one or more inert gases. Alternatively, the

tube may be open to a flow of the one or more organic compounds in gaseous form and optionally nitrogen and/or one or more inert gases.

Advantageously, the reaction temperature is maintained for between 0.5 and 12 hours, although the exact time will depend on the reactivity of the starting materials. Between 0.5 and 8 hours has been found to be sufficient for many reactions utilising the process of the present invention.

The amount of organic compound in gaseous form needed to perform the process of the present invention depends on the number of electrons being gained by the metal M during the reaction process.

The alkali metal (metal)-containing materials of formula $A_aM_b(X_cY_d)_eZ_f$ prepared by the process of the present invention are suitable for use in many different applications, for example as the active material in electrodes, particularly cathodes used in energy storage devices, rechargeable batteries, electrochemical devices and electrochromic devices. Advantageously, the electrodes made using the materials produced by the present invention are used in conjunction with a counter electrode and one or more electrolyte materials. The electrolyte materials may be any conventional or known materials and may comprise either aqueous electrolyte(s) or non-aqueous electrolyte(s).

An inherent problem with most alkali metal (metal)-containing compounds is their low electrical conductivity. To address this problem it is known to add conductive materials such as carbon-containing materials for example, graphite, carbon black, sucrose and acetylene black either to the starting materials, such as during grinding, or as a coating to the final metal-containing products. Other known conductive materials include metal powders and other highly conductive inorganic materials.

It is therefore desirable, when making inherently non-conductive alkali metal-containing compounds using the process of the present invention, to add one or more conductive materials to the reaction mixture and/or to one or more of the precursor compounds and/or to the final product.

Notwithstanding the above, another particularly useful advantage of the process of the present invention which uses one or more organic compounds in gaseous form, is that the reaction can, under temperature conditions below the organic compound pyrolysis temperature, advantageously produce $A_aM_b(X_cY_d)_eZ_f$ compounds which exhibit better

electrochemical results than would be expected for similar compounds made using other methods of production. As discussed above, it is usually the case that to obtain a high specific capacity material with low voltage polarization, that is voltage hysteresis between the charge and discharge processes, it is necessary for the electrode material to include intimately dispersed conductive material such as carbon, either during the synthesis step (for example by a carbothermal process) or by the use of a secondary carbon coating process. However, the Applicant has found that there is no need to add a separate conductive material to the compounds produced by the process of the present invention.

Consequently the Applicant has found that even at reaction temperatures below below the pyrolysis temperature of the one or more organic compounds, $A_aM_b(X_cY_d)_eZ_f$ compounds are produced in conjunction with (i.e. in situ) during the reaction between the precursor compounds and the one or more organic compounds gaseous form. Organic compounds such as ethanol and isopropyl alcohol in gaseous form are particularly efficient at depositing a layer of conductive material on the target alkali metal (metal)-containing compound.

Thus in a second aspect, the present invention provides a process for making a composition comprising a) an alkali metal (metal)-containing compound e.g. of the formula $A_aM_b(X_cY_d)_eZ_f$ as defined above, and b) one or more conductive materials, wherein at least a portion of the conductive materials is formed in situ during the process. The one or more conductive materials may comprise for example carbon or Fe_2P.

In a third aspect, the present invention provides an electrode which utilises active materials of formula $A_aM_b(X_cY_d)_eZ_f$, prepared in accordance with the present invention as described above, especially an electrode which utilises a composition comprising such active materials in combination with one or more conductive materials which are obtained, at least in part, during the reaction process described above involving one or more organic compounds in gaseous form.

In still further aspects, the present invention provides an energy storage device comprising an electrode as described above, for use as one or more of the following: a sodium ion and/or lithium ion and/or potassium ion cell; a sodium metal and/ or lithium metal and/or potassium metal ion cell; a non-aqueous electrolyte sodium ion and/or lithium ion and/or potassium ion cell; and an aqueous electrolyte sodium ion and/or lithium ion and/or potassium ion cell. Specifically, the energy storage device may be a battery.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will now be described with reference to the following figures in which:

FIGURE 1A shows the voltage profile (electrode potential versus cumulative specific capacity) for $LiFePO_4$ cathode active material (X0627a) produced according to Example 1 of the present invention;

FIGURE 1B shows the differential capacity profile (differential capacity versus electrode potential) for $LiFePO_4$ active material (X0627a) produced according to Example 1 of the present invention;

FIGURE 1C is an XRD profile for $LiFePO_4$ active material (X0627a) produced according to Example 1 of the present invention, the asterisks denote the main peak positions for the impurity phase $Li_3Fe_2(PO_4)_3$;

FIGURE 2A shows the voltage profile (electrode potential versus cumulative specific capacity) for $LiFePO_4$ active material (X1101) produced according to Example 2 of the present invention;

FIGURE 2B shows the differential capacity profile (differential capacity versus electrode potential) for $LiFePO_4$ active material (X1101) produced according to Example 2 of the present invention;

FIGURE 2C is an XRD profile for $LiFePO_4$ active material (X1101) produced according to Example 2 of the present invention;

FIGURE 3A shows the voltage profile (electrode potential versus cumulative specific capacity) for $LiFePO_4$ active material (X0856) produced according to Example 3 of the present invention;

FIGURE 3B shows the differential capacity profile (differential capacity versus electrode potential) for $LiFePO_4$ active material (X0856) produced according to Example 3 of the present invention;

FIGURE 3C is an XRD profile for $LiFePO_4$ active material (X0856) produced according to Example 3 of the present invention;

FIGURE 4A shows the voltage profile (electrode potential versus cumulative specific capacity) for $LiFePO_4$ active material (X0743) produced according to Example 4 of the present invention;

FIGURE 4B shows the differential capacity profile (differential capacity versus electrode potential) for $LiFePO_4$ active material (X0743) produced according to Example 4 of the present invention;

FIGURE 4C is an XRD profile for $LiFePO_4$ active material (X0743) produced according to Example 4 of the present invention;

FIGURE 5A shows the voltage profile (electrode potential versus cumulative specific capacity) for $LiFePO_4$ active material (X0650) produced according to Example 5 (comparative);

FIGURE 5B shows the differential capacity profile (differential capacity versus electrode potential) for $LiFePO_4$ active material (X0650) produced according to Example 5 (comparative);

FIGURE 5C is an XRD profile for $LiFePO_4$ active material (X0650) produced according to Example 5 (comparative);

FIGURE 6A shows the voltage profile (electrode potential versus cumulative specific capacity) for $LiFePO_4$ active material (X0649) produced according to Example 6 (comparative);

FIGURE 6B shows the differential capacity profile (differential capacity versus electrode potential) for $LiFePO_4$ active material (X0649) produced according to Example 6 (comparative);

FIGURE 6C is an XRD profile for $LiFePO_4$ active material (X0649) produced according to Example 6 (comparative);

FIGURE 7A shows the voltage profile (electrode potential versus cumulative specific capacity) for $NaFePO_4$ active material (X0934) produced according to Example 7 of the present invention;

FIGURE 7B shows the differential capacity profile (differential capacity versus electrode potential) for $NaFePO_4$ active material (X0934) produced according to Example 7 of the present invention;

FIGURE 7C is an XRD profile for $NaFePO_4$ active material (X0934) produced according to Example 7 of the present invention;

FIGURE 8A shows the voltage profile (electrode potential versus cumulative specific capacity) for $Li_3V_2(PO_4)_3$ active material (X0949) produced according to Example 8 of the present invention;

FIGURE 8B shows the differential capacity profile (differential capacity versus electrode potential) for $Li_3V_2(PO_4)_3$ active material (X0949) produced according to Example 8 of the present invention;

FIGURE 8C is an XRD profile for $Li_3V_2(PO_4)_3$ active material (X0949) produced according to Example 8 of the present invention;

FIGURE 9A shows the voltage profile (electrode potential versus cumulative specific capacity) for $Na_3V_2(PO_4)_3$ active material (X0945) produced according to Example 9 of the present invention;

FIGURE 9B shows the differential capacity profile (differential capacity versus electrode potential) for $Na_3V_2(PO_4)_3$ active material (X0945) produced according to Example 9 of the present invention;

FIGURE 9C is an XRD profile for $Na_3V_2(PO_4)_3$ active material (X0945) produced according to Example 9 of the present invention, the asterisks denote the main peak positions for the impurity phase, $NaVP_2O_7$

.

DETAILED DESCRIPTION

PREFERRED GENERAL METHOD:

1) Intimately mix together the precursor compounds in the correct stoichiometric ratio, remove the solvent if used, and press into a pellet.

2) Heat the resulting mixture of precursor compounds under an inert atmosphere consisting of one or more organic compounds in gaseous form and optionally nitrogen and/or one or more inert gases, in a furnace at a furnace temperature of between 150°C and 800°C until reaction product forms.

3) Allow the product to cool before grinding it to a powder.

The starting materials and reaction conditions used in the Examples 1 to 9 are summarised in Table 1 below:

TABLE 1

EXAMPLE	STARTING MATERIALS	TARGET PRODUCT	REACTION CONDITIONS
1	1.0 LiH_2PO_4 0.5 Fe_2O_3	$LiFePO_4$ (sample X0627a, cell#207017) XRD scan parameters:2θ=5°-60° Increment: 0.025° Speed: 1 sec/step	Mixing solvent: None. Organic compound: Ethanol vapour in flowing N_2. Heating temp. 400°C, Reaction time 4 hours, Ground, repelletised, heated at 450°C, for 3 hours.
2	0.5 Li_2CO_3 1 $FePO_4$	$LiFePO_4$ (sample X01101, Cell #303067) XRD scan parameters:2θ=5°-60° Increment: 0.025° Speed: 1 sec/step	Mixing solvent: Acetone. Organic compound: Ethanol vapour in flowing N_2 when T≥300°C Heating temp. 400°C, Reaction time 4 hours.
3	0.5 Li_2CO_3 1.0 $FePO_4$ ($FePO_4$ made by dehydrating $FePO_4.2H_2O$ at 400°C in air for 16	$LiFePO_4$ (sample X0856, Cell #210027) XRD scan	Mixing solvent: Acetone. Organic compound: Ethanol vapour in flowing N_2

	hours)	parameters:2θ=5°-60° Increment: 0.025° Speed: 1 sec/step	Heating temp.550°C, Reaction time 6 hours.
4	1.0 LiH_2PO_4 0.5 Fe_2O_3	$LiFePO_4$ (sample X0743, Cell # 2089011) XRD scan parameters:2θ=5°-60° Increment: 0.025° Speed: 1 sec/step	Mixing solvent: Acetone. Organic compound: isopropanol vapour in flowing N_2 Heating temp. 600°C, Reaction time 4 hours.
5 **(Comparative)**	1.0 LiH_2PO_4 1.0 $Fe(C_2O_4).2H_2O$	$LiFePO_4$ (sample X0650, Cell #207072) XRD scan parameters:2θ=5°-60° Increment: 0.025° Speed: 1 sec/step	Mixing solvent: None. Reaction conditions: N_2, 750°C, dwell time of 8 hours.
6 **(Comparative)**	1.0 LiH_2PO_4 0.5 Fe_2O_3 0.625 C	$LiFePO_4$ (sample X0649, Cell #207071) XRD scan parameters:2θ=5°-60° Increment: 0.025° Speed: 1 sec/step	Mixing solvent: None Reaction conditions: N_2, 750°C, dwell time of 8 hours.
7	1 NaH_2PO_4 0.5 Fe_2O_3	$NaFePO_4$ (sample X0934, Cell # 211019) XRD scan parameters:2θ=5°-60° Increment: 0.025° Speed: 1 sec/step	Mixing solvent: Acetone Organic compound: Ethanol vapour in flowing N_2 Reaction temp. 750°C Reaction time 6 hours.
8	3.0 LiH_2PO_4 1.0 V_2O_5	$Li_3V_2(PO_4)_3$ (sample X0949, Cell # 211039) XRD scan parameters:2θ=5°-60° Increment: 0.025° Speed: 1 sec/step	Mixing solvent: Acetone Organic compound: Ethanol vapour in flowing N_2 when furnace temp. ≥500°C Reaction temp 800°C, Reaction time 6 hours.

9	3.0 NaH_2PO_4 1.0 V_2O_5	$Na_3V_2(PO_4)_3$ (sample X0945 Cell # 211033) XRD scan parameters:2θ=5°-60° Increment: 0.025° Speed: 1 sec/step	Mixing solvent: Acetone Organic compound: Ethanol vapour in flowing N_2 Reaction temp. 500°C, Reaction time 8 hours.

Product Analysis using XRD

Analysis by X-ray diffraction techniques was conducted using a Siemens D5000 powder diffractometer to confirm that the desired target materials had been prepared, to establish the phase purity of the product material and to determine the types of impurities present. From this information it is possible to determine the unit cell lattice parameters.

The general XRD operating conditions used to analyse the precursor electrode materials are as follows:

Slits sizes: 1 mm, 1 mm, 0.1 mm

Range: 2θ = 5 ° - 60 °

X-ray Wavelength = 1.5418 Å (Cu Kα)

Speed: 0.5 to 2 seconds/step

Increment: 0.015° to 0.05 °

Electrochemical Results

The target materials were tested in a metallic lithium half cell which can be made using the following procedure:

Generic Procedure to Make a Lithium Metal Electrochemical Test Cell

The positive electrode is prepared by solvent-casting a slurry of the active material, conductive carbon, binder and solvent. The conductive carbon used is Super P (Timcal). PVdF co-polymer (e.g. Kynar Flex 2801, Elf Atochem Inc.) is used as the binder, and acetone is employed as the solvent. The slurry is then cast onto glass and a free-standing electrode film is formed as the solvent evaporates. The electrode is then dried further at about 80°C. The electrode film contains the following components, expressed in percent by weight: 80% active material, 8% Super P carbon, and 12% Kynar 2801 binder.

Optionally, an aluminium current collector may be used to contact the positive electrode. Metallic lithium on a copper current collector may be employed as the negative electrode. The electrolyte comprises one of the following: (i) a 1 M solution of $LiPF_6$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) in a weight ratio of 1:1; (ii) a 1 M solution of $LiPF_6$ in ethylene carbonate (EC) and diethyl carbonate (DEC) in a weight ratio of 1:1; or (iii) a 1 M solution of $LiPF_6$ in propylene carbonate (PC). A glass fibre separator (Whatman, GF/A) or a porous polypropylene separator (e.g. Celgard 2400) wetted by the electrolyte is interposed between the positive and negative electrodes.

Cell Testing

The cells are tested as follows, using Constant Current Cycling techniques.
The cell is cycled at a given current density between pre-set voltage limits. A commercial battery cycler from Maccor Inc. (Tulsa, OK, USA) is used. On charge, lithium (sodium)-ions are extracted from the cathode active material. During discharge, lithium (sodium)-ions are re-inserted into the cathode active material.

EXAMPLE 1

Figures 1A and 1B (Cell#207017) show the first cycle constant current cycling data for the $LiFePO_4$ cathode active material (X0627a, made using ethanol vapour as the organic compound in gaseous form, first at 400°C then at 450°C), measured in a metallic lithium half-cell. Figure 1A shows the voltage profile (electrode potential versus cumulative specific capacity) and Figure 1B shows the differential capacity profile (differential capacity versus electrode potential). The constant current data shown in the figure were collected using a lithium metal counter electrode at a current density of 0.04 mA/cm^2 between voltage limits of 2.5 and 4.2 V. The non-aqueous electrolyte used was a 1 M solution of $LiPF_6$ in a 1:1 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The electrochemical testing was carried out at a controlled temperature of 25°C.

The Open Circuit Voltage (OCV) of the as-made cell was 3.273 V vs. Li. Referring to Figure 1A, during the first lithium extraction process, a charge equivalent to a material specific capacity of 110 mAh/g was obtained for the cathode active material. The subsequent re-insertion process corresponded to material specific capacity of 100 mAh/g, indicating the general reversibility of the lithium-ion insertion reactions.

The symmetrical nature of the charge-discharge voltage profile indicates the excellent reversibility of the system. This is further exemplified by the symmetrical nature of the differential capacity profile shown in Figure 1B.

EXAMPLE 2

Figures 2A and 2B (Cell#303067) show the first cycle constant current cycling data for the $LiFePO_4$ cathode active material (X1101, made using ethanol vapour as the organic compound in gaseous form at 400°C) measured in a metallic lithium half-cell. Figure 2A shows the voltage profile (electrode potential versus cumulative specific capacity) and Figure 2B shows the differential capacity profile (differential capacity versus electrode potential). The constant current data shown in the figure were collected using a lithium metal counter electrode at a current density of 0.04 mA/cm^2 between voltage limits of 2.5 and 4.2 V. The non-aqueous electrolyte used was a 1 M solution of $LiPF_6$ in a 1:1 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The electrochemical testing was carried out at a controlled temperature of 25°C.

The Open Circuit Voltage (OCV) of the as-made cell was 3.073 V vs. Li. Referring to Figure 2A, during the first lithium extraction process, a charge equivalent to a material specific capacity of 100 mAh/g was obtained for the cathode active material. The subsequent re-insertion process corresponded to material specific capacity of 86 mAh/g, indicating the general reversibility of the lithium-ion insertion reactions.

The symmetrical nature of the charge-discharge voltage profile indicates the excellent reversibility of the system. This is further exemplified by the symmetrical nature of the differential capacity profile shown in Figure 2B.

EXAMPLE 3

Figures 3A and 3B (Cell#210027) show the first cycle constant current cycling data for the $LiFePO_4$ cathode active material (X0856, made using ethanol vapour as the organic compound in gaseous form at 550°C) measured in a metallic lithium half-cell. Figure 3A shows the voltage profile (electrode potential versus cumulative specific capacity) and Figure 3B shows the differential capacity profile (differential capacity versus electrode potential). The constant current data shown in the figure were collected using a lithium metal counter electrode at a current density of 0.04 mA/cm^2 between voltage limits of 2.5 and 4.2 V. The non-aqueous electrolyte used was a 1 M solution of $LiPF_6$ in a 1:1 mixture

of ethylene carbonate (EC) and diethyl carbonate (DEC). The electrochemical testing was carried out at a controlled temperature of 25°C.

The Open Circuit Voltage (OCV) of the as-made cell was 3.078 V vs. Li. Referring to Figure 3A, during the first lithium extraction process, a charge equivalent to a material specific capacity of 115 mAh/g was obtained for the cathode active material. The subsequent re-insertion process corresponded to material specific capacity of 90 mAh/g, indicating the general reversibility of the lithium-ion insertion reactions.

The symmetrical nature of the charge-discharge voltage profile indicates the excellent reversibility of the system. This is further exemplified by the symmetrical nature of the differential capacity profile shown in Figure 3B.

EXAMPLE 4

Figures 4A and 4B (Cell#2089011) show the first cycle constant current cycling data for the $LiFePO_4$ cathode active material (X0743, made using isopropanol vapour as the organic compound in gaseous form at 650°C) measured in a metallic lithium half-cell. Figure 4A shows the voltage profile (electrode potential versus cumulative specific capacity) and Figure 4B shows the differential capacity profile (differential capacity versus electrode potential). The constant current data shown in the figure were collected using a lithium metal counter electrode at a current density of 0.04 mA/cm^2 between voltage limits of 2.5 and 4.2 V. The non-aqueous electrolyte used was a 1 M solution of $LiPF_6$ in a 1:1 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The electrochemical testing was carried out at a controlled temperature of 25°C.

The Open Circuit Voltage (OCV) of the as-made cell was 3.934 V vs. Li. Referring to Figure 4A, during the first lithium extraction process, a charge equivalent to a material specific capacity of 111 mAh/g was obtained for the cathode active material. The subsequent re-insertion process corresponded to material specific capacity of 107 mAh/g, indicating the general reversibility of the lithium-ion insertion reactions.

The symmetrical nature of the charge-discharge voltage profile indicates the excellent reversibility of the system. This is further exemplified by the symmetrical nature of the differential capacity profile shown in Figure 4B.

EXAMPLE 5 (Comparative)

Figures 5A and 5B (Cell#207072) show the first cycle constant current data for the $LiFePO_4$ cathode active material (X0650, made from iron oxalate, $Fe(C_2O_4).2H_2O$ – an Fe^{2+} precursor that requires no reducing agent) measured in a metallic lithium half-cell. Figure 5A shows the voltage profile (electrode potential versus cumulative specific capacity) and Figure 5B shows the differential capacity profile (differential capacity versus electrode potential). The constant current data shown in the figure were collected using a lithium metal counter electrode at a current density of 0.04 mA/cm^2 between voltage limits of 2.5 and 4.2 V. The non-aqueous electrolyte used was a 1 M solution of $LiPF_6$ in a 1:1 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The electrochemical testing was carried out at a controlled temperature of 25°C.

The Open Circuit Voltage (OCV) of the as-made cell was 3.177 V vs. Li. Referring to Figure 5A, during the first lithium extraction process, a charge equivalent to a material specific capacity of 63 mAh/g was obtained for the cathode active material. This is a relatively low material utilization. The subsequent re-insertion process corresponded to material specific capacity of 45 mAh/g indicating the relatively poor reversibility. Figure 5B shows the corresponding differential capacity profile for this material which is indistinct and noisy indicating the poor electrochemical reversibility of the active material.

EXAMPLE 6 (Comparative)

Figures 6A and 6B (Cell#207071) show the first cycle constant current data for the $LiFePO_4$ cathode active material (X0649, made from Fe_2O_3 by carbothermal reduction using Super P Carbon (Timcal) as the reducing agent and conductivity enhancer) measured in a metallic lithium half-cell. Figure 6A shows the voltage profile (electrode potential versus cumulative specific capacity) and Figure 6B shows the differential capacity profile (differential capacity versus electrode potential). The constant current data shown in the figure were collected using a lithium metal counter electrode at a current density of 0.04 mA/cm^2 between voltage limits of 2.5 and 4.2 V. The non-aqueous electrolyte used was a 1 M solution of $LiPF_6$ in a 1:1 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The electrochemical testing was carried out at a controlled temperature of 25°C.

The Open Circuit Voltage (OCV) of the as-made cell was 3.177 V vs. Li. Referring to Figure 5A, during the first lithium extraction process, a charge equivalent to a material

specific capacity of 135 mAh/g was obtained for the cathode active material. The subsequent re-insertion process corresponded to material specific capacity of 111mAh/g indicating good reversibility.

The symmetrical nature of the charge-discharge voltage profile further indicates the reversibility of the system. This is further exemplified by the symmetrical nature of the differential capacity profile shown in Figure 6B.

EXAMPLE 7

Figures 7A and 7B (Cell#211019) show the first cycle constant current data for the $NaFePO_4$ cathode active material (X0934, made using the ethanol vapour at 500°C as the organic compound in gaseous form) measured in a metallic lithium half-cell. Figure 7A shows the voltage profile (electrode potential versus cumulative specific capacity) and Figure 7B shows the differential capacity profile (differential capacity versus electrode potential). The constant current data shown in the figure were collected using a lithium metal counter electrode at a current density of 0.04 mA/cm^2 between voltage limits of 2.0 and 4.0 V. The non-aqueous electrolyte used was a 1 M solution of $LiPF_6$ in a 1:1 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The electrochemical testing was carried out at a controlled temperature of 25°C.

The Open Circuit Voltage (OCV) of the as-made cell was 2.902 V vs. Li. Referring to Figure 7A, it is assumed that sodium ions are extracted from the active material during the initial charging of the cell. During the sodium ion extraction process, a charge equivalent to a material specific capacity of 28 mAh/g was obtained for the cathode active material. It is expected from thermodynamic considerations that the sodium extracted from the $NaFePO_4$ material during the initial charging process, enters the electrolyte, and is then displacement 'plated' onto the lithium metal anode (i.e. releasing more lithium into the electrolyte). Therefore, during the subsequent discharging of the cell, it is assumed that a mix of lithium and sodium is re-inserted into the material. The re-insertion process corresponds to 47mAh/g, indicating the reversibility of the ion insertion reactions.

The symmetrical nature of the charge-discharge voltage profile indicates the reversibility of the system. This is further exemplified by the symmetrical nature of the differential capacity profile shown in Figure 7B.

EXAMPLE 8

Figures 8A and 8B (Cell#211039) show the first cycle constant current data for the $Li_3V_2(PO_4)_3$ cathode active material (X0949, made using ethanol vapour at 800°C as the organic compound in gaseous form) measured in a metallic lithium half-cell. Figure 8A shows the voltage profile (electrode potential versus cumulative specific capacity) and Figure 8B shows the differential capacity profile (differential capacity versus electrode potential). The constant current data shown in the figure were collected using a lithium metal counter electrode at a current density of 0.04 mA/cm^2 between voltage limits of 2.0 and 4.3 V. The non-aqueous electrolyte used was a 1 M solution of $LiPF_6$ in a 1:1 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The electrochemical testing was carried out at a controlled temperature of 25°C.

The Open Circuit Voltage (OCV) of the as-made cell was 1.980 V vs. Li. Referring to Figure 8A, during the first lithium extraction process, a charge equivalent to a material specific capacity of 119 mAh/g was obtained for the cathode active material. The subsequent re-insertion process corresponded to material specific capacity of 104 mAh/g, indicating the general reversibility of the lithium-ion insertion reactions.

The symmetrical nature of the charge-discharge voltage profile indicates the reversibility of the system. This is further exemplified by the symmetrical nature of the differential capacity profile shown in Figure 8B.

EXAMPLE 9

Figures 9A and 9B (Cell#211033) show the first cycle constant current data for the $Na_3V_2(PO_4)_3$ cathode active material (X0945, made using ethanol vapour at 700°C as the organic compound in gaseous form) measured in a metallic lithium half-cell. Figure 9A shows the voltage profile (electrode potential versus cumulative specific capacity) and Figure 9B shows the differential capacity profile (differential capacity versus electrode potential). The constant current data shown in the figure were collected using a lithium metal counter electrode at a current density of 0.04 mA/cm^2 between voltage limits of 2.5 and 4.0 V. The non-aqueous electrolyte used was a 1 M solution of $LiPF_6$ in a 1:1 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The electrochemical testing was carried out at a controlled temperature of 25°C.

The Open Circuit Voltage (OCV) of the as-made cell was 2.112 V vs. Li. Referring to Figure 9A, it is assumed that sodium ions are extracted from the $Na_3V_2(PO_4)_3$ active material during the initial charging of the cell. During the sodium ion extraction process, a charge equivalent to a material specific capacity of 83 mAh/g was obtained for the cathode active material. It is expected from thermodynamic considerations that the sodium extracted from the material during the initial charging process, enters the electrolyte, and is then displacement 'plated' onto the lithium metal anode (i.e. releasing more lithium into the electrolyte). Therefore, during the subsequent discharging of the cell, it is assumed that a mix of lithium and sodium is re-inserted into the material. The re-insertion process corresponds to 24 mAh/g, indicating the reversibility of the ion insertion reactions.

The symmetrical nature of the charge-discharge voltage profile indicates the reversibility of the system. This is further exemplified by the symmetrical nature of the differential capacity profile shown in Figure 9B.

EXAMPLE 10: A Demonstration of the Fate of the Organic Compounds in Gaseous Form during the Process of the Present Invention.

The following experiment demonstrates what happens to ethanol when it is used as the organic compound in gaseous form in the process of the present invention.

Experimental method

The following method uses the same precursor mixture and reaction conditions as those described above in Example 4.

A mixture of the precursor compounds LiH_2PO_4 and Fe_2O_3, in a 2:1 ratio, was placed in a tube furnace. Ethanol in gaseous form entrained in flowing N_2, was passed over this mixture at 600 °C, for 4 hours.

A Dreschel bottle, packed in ice, was placed on the outlet of the furnace tube, to condense and trap any reacted and unreacted ethanol vapour that had been passed over the mixture containing the two or more precursor compounds. Once allowed to reach room temperature, the collected condensate was analysed for pH and density and compared to those of ethanol as received from the supplier.

Results

The liquid collected in the outlet Dreschel bottle during this experiment had significantly increased in density and reduced in pH relative to ethanol (as shown in the table below). These results are consistent with at least partial oxidation of ethanol to ethanoic acid, caused during the reduction of at least part of the reaction mixture.

TABLE 2

	Input Dreschel			Output Dreschel	
Contents	**Expected Density (g/cm^3)**	**Measured Density (g/cm^3)**	**Measured pH**	**Measured Density (g/cm^3)**	**Measured pH**
Ethanol	0.789	0.792	5	0.9955	2.5

Densities of possible reactants/products in output Dreschel bottle: -

Ethanol: 0.789 g/cm^3

Ethanoic acid: 1.050 g/cm^3

Conclusion

The liquid collected in the Dreschel bottle is a mixture of ethanol and a high percentage of ethanoic acid. This is in contrast to the process described for example in US2007/0134554A which describes that the organic compounds such as cellulose acetate, must be broken down under the conditions of the reaction of the prior art to yield the pyrolysis products carbon, carbon monoxide, ammonia and hydrogen gas, prior to their reaction with the precursor compounds.

CLAIMS:

1. A solid state process for the preparation of an alkali metal (metal)-containing compound comprising i) forming a mixture comprising two or more precursor compounds, at least one of which comprises at least one alkali metal, and ii) heating the mixture comprising the two or more precursor compounds under an atmosphere consisting of one or more organic compounds in gaseous form and optionally nitrogen and/or one or more inert gases, wherein the one or more organic compounds in gaseous form are selected from aliphatic alcohols, aldehydes, carboxylic acids, ketones, glyoxylic acid, dimethyl aminoborane and trimethyl aminoborane.

2. A solid state process for preparing an alkali metal (metal)-containing compound according to claim 1 wherein the alkali metal (metal)-containing compound is of the formula:

$A_aM_b(X_cY_d)_eZ_f$

wherein:

A is an alkali metal selected from one or more of lithium, sodium and potassium;

M comprises one or more metals selected from transition metals and/or non-transition metals and/or metalloids;

$(X_cY_d)_e$ is at least one first anion; and

Z is at least one second anion

wherein $a > 0$; $b > 0$; $c > 0$; $d \geq 0$; $e > 0$ and $f \geq 0$;

wherein a, b, c, d, e and f are chosen to maintain electroneutrality.

3. A solid state process according to claim 1 or 2 wherein one or more of the precursor compounds comprises at least one transition metal which is reduced by the one or more organic compounds in gaseous form.

4. A solid state process according to claim 2 wherein M is selected from one or more of titanium, vanadium, niobium, tantalum, hafnium, chromium, molybdenum, tungsten, manganese, iron, osmium, cobalt, nickel, palladium, platinum, copper, silver, gold, zinc, cadmium, aluminium, scandium, yttrium, zirconium, technetium, rhenium, ruthenium, rhodium, iridium, mercury, gallium, indium, tin, lead, bismuth, magnesium, calcium , beryllium, strontium, barium, boron, silicon, germanium, arsenic, antimony and tellurium.

5. A solid state process according to claim 2 wherein X comprises one or more elements selected from titanium, vanadium, chromium, arsenic, molybdenum, tungsten, niobium, manganese, aluminium, selenium, boron, oxygen, carbon, silicon, phosphorus, nitrogen, sulfur, fluorine, chlorine, bromine and iodine.

6. A solid state process according to claim 2 wherein Y is selected from one or more halides, sulfur-containing groups, oxygen-containing groups and mixtures thereof.

7. A solid state process according to claim 2 wherein Z is selected from one or more halides, hydroxide-containing groups and mixtures thereof.

8. A solid state process according to claim 2 wherein X comprises phosphorus.

9. A solid state process according to claim 8 wherein $(X_cY_d)_e$ is a PO_4 and/or P_2O_7 moiety.

10. A solid state process according to claim 2 wherein X comprises sulfur.

11. A solid state process according to claim 10 wherein $(X_cY_d)_e$ is a SO_4 moiety.

12. A solid state process according to claims 1 to 11 for preparing materials comprising $LiFePO_4$, $LiFePO_4/Fe_2P$, $LiMnPO_4$, $LiCoPO_4$, $LiNiPO_4$, $NaFePO_4$, $NaMnPO_4$, $NaCoPO_4$, $NaNiPO_4$, $LiMn_{0.5}Fe_{0.2}Mg_{0.3}PO_4$, $Li_3V_2(PO_4)_3$, $Na_4Fe_3(PO_4)_2P_2O_7$, $Na_3V_2(PO_4)_3$, $LiMn_{0.5}Fe_{0.5}PO_4$, $Na_7V_4(P_2O_7)_4PO_4$, $Na_7V_3(P_2O_7)_4$, $Na_2Fe(SO_4)_2$, $NaVPO_4F$, $LiVPO_4F$, Na_xMnO_2, $Na_3V(PO_4)_2$, $Li_3V(PO_4)_2$, $NaVOPO_4$, $LiVOPO_4$, LiV_2O_5, NaV_2O_5, $NaVO_2$, $Na_{8-2x}Fe_{4+x}(P_2O_7)_4$, $Na_{8-2x}Mn_{4+x}(P_2O_7)_4$, $Na_2MnP_2O_7$, $Na_2FeP_2O_7$, $Na_2CoP_2O_7$, $Na_4Mn_3(PO_4)_2P_2O_7$, $Na_4Co_3(PO_4)_2P_2O_7$, $Na_4Ni_3(PO_4)_2P_2O_7$, $NaFeSO_4F$, $LiFeSO_4F$, $NaMnSO_4F$, $LiMnSO_4F$, $Na_2Fe_2(SO_4)_3$, $Li_2Fe_2(SO_4)_3$, $Li_2Fe(SO_4)_2$, Na_2FePO_4F, Na_2MnPO_4F, Na_2CoPO_4F and Na_2NiPO_4F.

13. A solid state process for preparing lithium metal phosphates of the general formula: $LiMPO_4$ where M is a metal selected from one or more of manganese, iron, cobalt, nickel, copper, zinc, magnesium and calcium, comprising i) forming a mixture of two or more precursor compounds and ii) heating the mixture of precursor compounds under an atmosphere consisting of one or more organic compounds in gaseous form and optionally nitrogen and/or one or more inert gases, wherein the one or more organic compounds in gaseous form are selected from aliphatic alcohols, aldehydes,

carboxylic acids, ketones, glyoxylic acid, dimethyl aminoborane and trimethyl aminoborane.

14. A solid state process according to any of claims 1 to 9, 12 and 13 for the preparation of $LiFePO_4$ comprising i) forming a mixture of two or more precursor compounds wherein the precursor compounds are selected from LiH_2PO_4, Fe_2O_3, Li_2CO_3, Li_2HPO_4, LiOH, $LiOH.H_2O$, Fe_3O_4, $FePO_4.xH_2O$, $FePO_4$, $Fe_3(PO_4)_2$, $FeSO_4.xH_2O$, $Fe(NO_3)_3.xH_2O$, $Fe(CH_3CO_2)_2$, $C_6H_8O_7.xFe^{3+}.yNH_3$ (ammonium iron (III) citrate), $C_6H_5FeO_7$ (iron (III) citrate), $Fe(C_5H_7O_2)_3$ (iron (III) 2,4-petanedionate), $Fe(C_2O_4).2H_2O$, P_2O_5 and H_3PO_4, and ii) heating the mixture of precursor compounds under an atmosphere consisting of one or more organic compounds in gaseous form and optionally nitrogen and/or one or more inert gases, wherein the one or more organic compounds in gaseous form are selected from aliphatic alcohols, aldehydes, carboxylic acids, ketones, glyoxylic acid, dimethyl aminoborane and trimethyl aminoborane.

15. A solid state process according to any of claims 1 to 14 further comprising the addition of one or more conductive materials.

16. A solid state process according to claims 1 to 15 for making a composition comprising:

a) a compound of formula $A_aM_b(X_cY_d)_eZ_f$; and

b) one or more conductive materials,

wherein at least a portion of the one or more conductive materials is formed in situ during the process.

17. A solid state process according to claim 16 wherein the at least one conductive material formed in situ comprises carbon derived from the precursor compounds and/or the one or more organic compounds in gaseous form.

AMENDED CLAIMS
received by the International Bureau on 06 October 2014 (06.10.2014)

1. A solid state process for the preparation of an alkali metal (metal)-containing compound comprising i) forming a mixture comprising two or more precursor compounds, wherein at least one precursor compound comprises at least one alkali metal, and at least one precursor compound comprises one or more metals selected from transition metals, non-transition metals and metalloids and ii) heating the mixture comprising the two or more precursor compounds under an atmosphere consisting of one or more organic compounds in gaseous form and optionally nitrogen and/or one or more inert gases, wherein the one or more organic compounds in gaseous form are selected from aliphatic alcohols, aldehydes, carboxylic acids, ketones, glyoxylic acid, dimethyl aminoborane and trimethyl aminoborane and wherein at least one of the one or more metals in at least one precursor compound is reduced by the one or more organic compounds in gaseous form.

2. A solid state process for preparing an alkali metal (metal)-containing compound according to claim 1 wherein the alkali metal (metal)-containing compound is of the formula:
$A_aM_b(X_cY_d)_eZ_f$
wherein:
A is an alkali metal selected from one or more of lithium, sodium and potassium;
M comprises one or more metals selected from transition metals and/or non-transition metals and/or metalloids;
$(X_cY_d)_e$ is at least one first anion; and
Z is at least one second anion
wherein $a > 0$; $b > 0$; $c > 0$; $d \geq 0$; $e > 0$ and $f \geq 0$;
wherein a, b, c, d, e and f are chosen to maintain electroneutrality.

3. A solid state process according to claim 1 or 2 wherein one or more of the precursor compounds comprises at least one transition metal which is reduced by the one or more organic compounds in gaseous form.

4. A solid state process according to claim 2 wherein M is selected from one or more of titanium, vanadium, niobium, tantalum, hafnium, chromium, molybdenum, tungsten, manganese, iron, osmium, cobalt, nickel, palladium, platinum, copper, silver, gold, zinc, cadmium, aluminium, scandium, yttrium, zirconium, technetium, rhenium, ruthenium, rhodium, iridium, mercury, gallium, indium, tin, lead, bismuth, magnesium,

AMENDED SHEET (ARTICLE 19)

calcium , beryllium, strontium, barium, boron, silicon, germanium, arsenic, antimony and tellurium.

5. A solid state process according to claim 2 wherein X comprises one or more elements selected from titanium, vanadium, chromium, arsenic, molybdenum, tungsten, niobium, manganese, aluminium, selenium, boron, oxygen, carbon, silicon, phosphorus, nitrogen, sulfur, fluorine, chlorine, bromine and iodine.

6. A solid state process according to claim 2 wherein Y is selected from one or more halides, sulfur-containing groups, oxygen-containing groups and mixtures thereof.

7. A solid state process according to claim 2 wherein Z is selected from one or more halides, hydroxide-containing groups and mixtures thereof.

8. A solid state process according to claim 2 wherein X comprises phosphorus.

9. A solid state process according to claim 8 wherein $(X_cY_d)_e$ is a PO_4 and/or P_2O_7 moiety.

10. A solid state process according to claim 2 wherein X comprises sulfur.

11. A solid state process according to claim 10 wherein $(X_cY_d)_e$ is a SO_4 moiety.

12. A solid state process according to claims 1 to 11 for preparing materials comprising $LiFePO_4$, $LiFePO_4/Fe_2P$, $LiMnPO_4$, $LiCoPO_4$, $LiNiPO_4$, $NaFePO_4$, $NaMnPO_4$, $NaCoPO_4$, $NaNiPO_4$, $LiMn_{0.5}Fe_{0.2}Mg_{0.3}PO_4$, $Li_3V_2(PO_4)_3$, $Na_4Fe_3(PO_4)_2P_2O_7$, $Na_3V_2(PO_4)_3$, $LiMn_{0.5}Fe_{0.5}PO_4$, $Na_7V_4(P_2O_7)_4PO_4$, $Na_7V_3(P_2O_7)_4$, $Na_2Fe(SO_4)_2$, $NaVPO_4F$, $LiVPO_4F$, Na_xMnO_2, $Na_3V(PO_4)_2$, $Li_3V(PO_4)_2$, $NaVOPO_4$, $LiVOPO_4$, LiV_2O_5, NaV_2O_5, $NaVO_2$, $Na_{8-2x}Fe_{4+x}(P_2O_7)_4$, $Na_{8-2x}Mn_{4+x}(P_2O_7)_4$, $Na_2MnP_2O_7$, $Na_2FeP_2O_7$, $Na_2CoP_2O_7$, $Na_4Mn_3(PO_4)_2P_2O_7$, $Na_4Co_3(PO_4)_2P_2O_7$, $Na_4Ni_3(PO_4)_2P_2O_7$, $NaFeSO_4F$, $LiFeSO_4F$, $NaMnSO_4F$, $LiMnSO_4F$, $Na_2Fe_2(SO_4)_3$, $Li_2Fe_2(SO_4)_3$, $Li_2Fe(SO_4)_2$, Na_2FePO_4F, Na_2MnPO_4F, Na_2CoPO_4F and Na_2NiPO_4F.

13. A solid state process for preparing lithium metal phosphates of the general formula: $LiMPO_4$ where M is a metal selected from one or more of manganese, iron, cobalt, nickel, copper, zinc, magnesium and calcium, comprising i) forming a mixture of two or more precursor compounds and ii) heating the mixture of precursor compounds under an atmosphere consisting of one or more organic compounds in gaseous form and

optionally nitrogen and/or one or more inert gases, wherein the one or more organic compounds in gaseous form are selected from aliphatic alcohols, aldehydes, carboxylic acids, ketones, glyoxylic acid, dimethyl aminoborane and trimethyl aminoborane.

14. A solid state process according to any of claims 1 to 9, 12 and 13 for the preparation of $LiFePO_4$ comprising i) forming a mixture of two or more precursor compounds wherein the precursor compounds are selected from LiH_2PO_4, Fe_2O_3, Li_2CO_3, Li_2HPO_4, LiOH, $LiOH.H_2O$, Fe_3O_4, $FePO_4.xH_2O$, $FePO_4$, $Fe_3(PO_4)_2$, $FeSO_4.xH_2O$, $Fe(NO_3)_3.xH_2O$, $Fe(CH_3CO_2)_2$, $C_6H_8O_7.xFe^{3+}.yNH_3$ (ammonium iron (III) citrate), $C_6H_5FeO_7$ (iron (III) citrate), $Fe(C_5H_7O_2)_3$ (iron (III) 2,4-petanedionate), $Fe(C_2O_4).2H_2O$, P_2O_5 and H_3PO_4, and ii) heating the mixture of precursor compounds under an atmosphere consisting of one or more organic compounds in gaseous form and optionally nitrogen and/or one or more inert gases, wherein the one or more organic compounds in gaseous form are selected from aliphatic alcohols, aldehydes, carboxylic acids, ketones, glyoxylic acid, dimethyl aminoborane and trimethyl aminoborane.

15. A solid state process according to any of claims 1 to 14 further comprising the addition of one or more conductive materials.

16. A solid state process according to claims 1 to 15 for making a composition comprising:

a) a compound of formula $A_aM_b(X_cY_d)_eZ_f$; and

b) one or more conductive materials,

wherein at least a portion of the one or more conductive materials is formed in situ during the process.

17. A solid state process according to claim 16 wherein the at least one conductive material formed in situ comprises carbon derived from the precursor compounds and/or the one or more organic compounds in gaseous form.

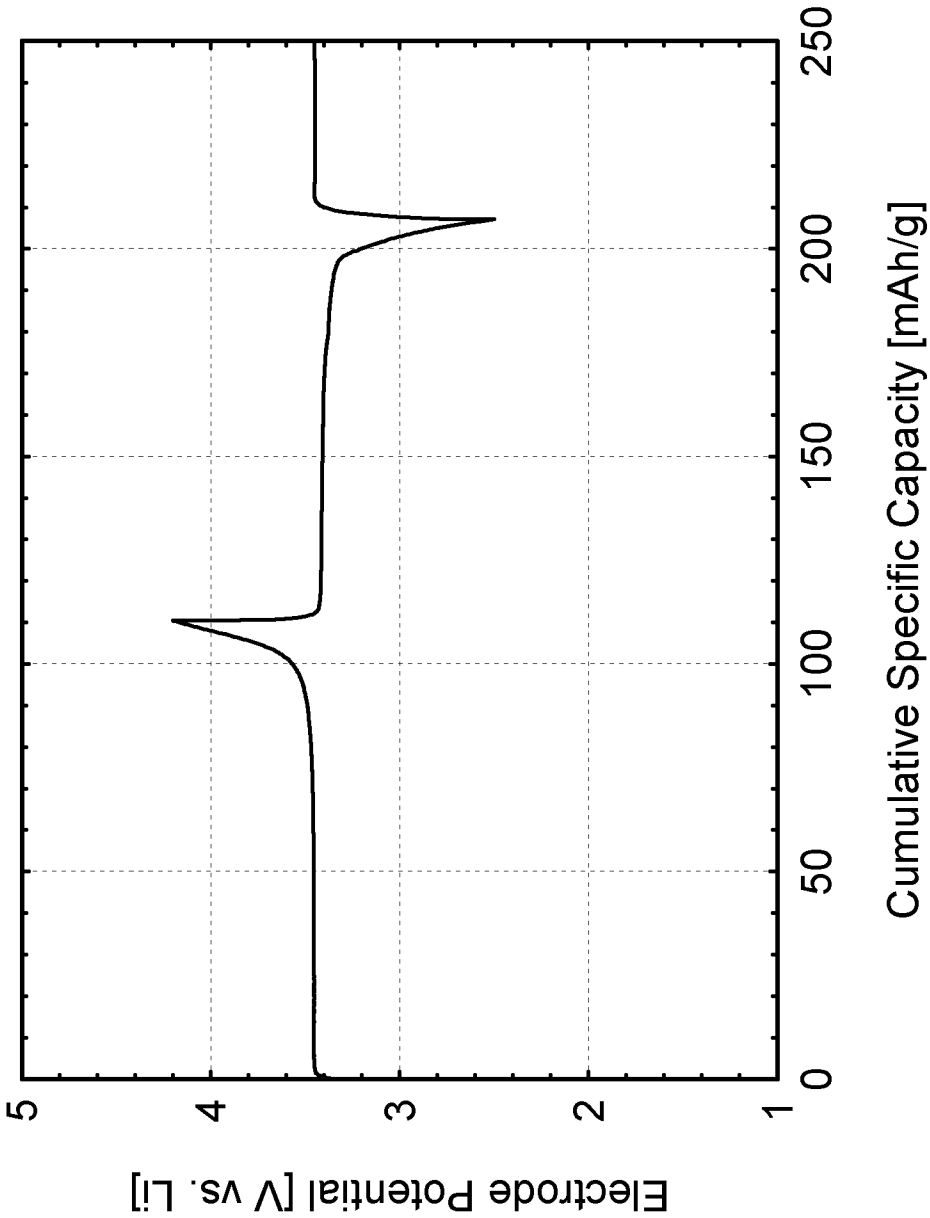
Electrode Potential [V vs. Li]
5
4
3
2
1
0
50
100
150
200
250
Cumulative Specific Capacity [mAh/g]

FIGURE 1A

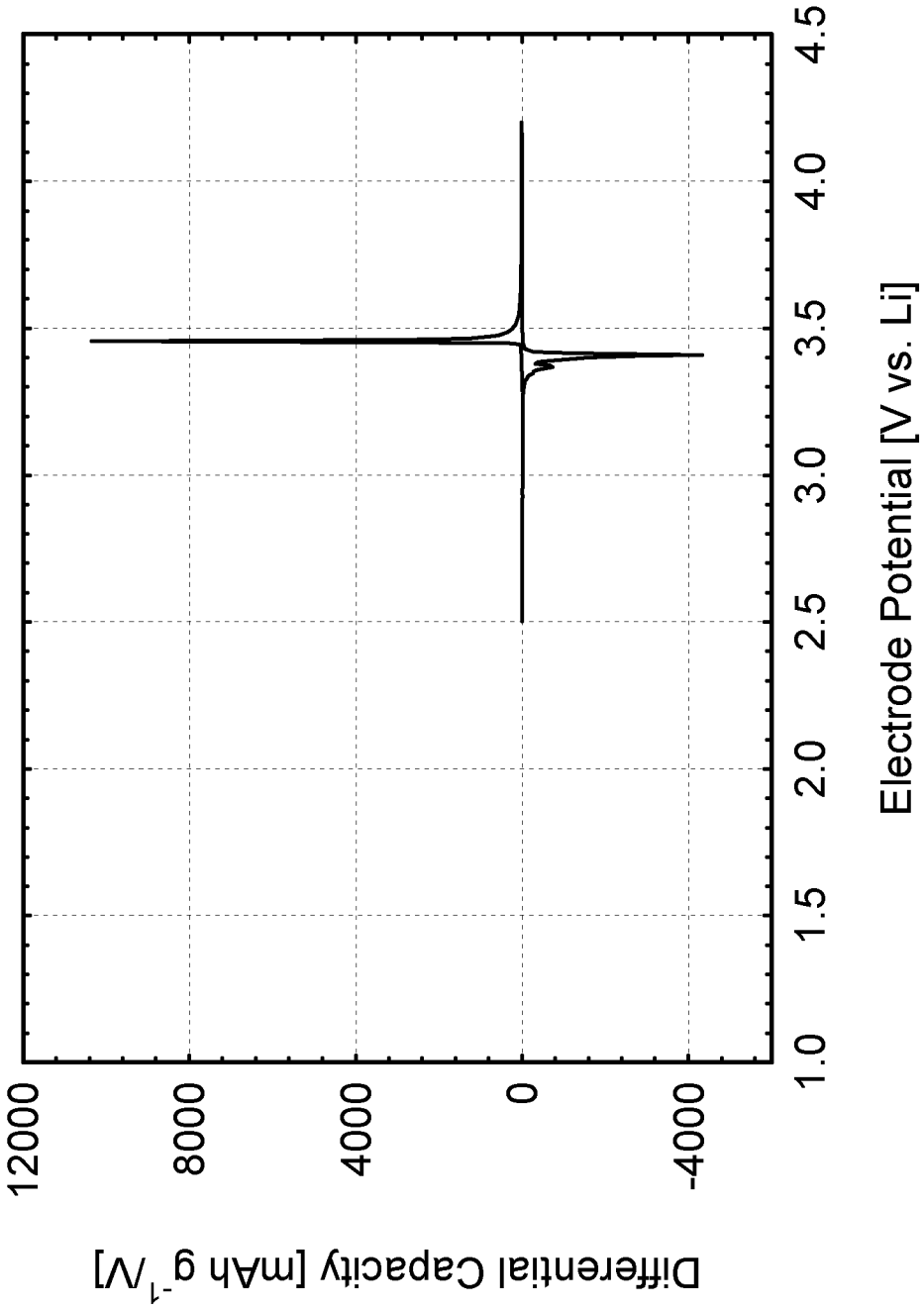
12000
8000
4000
0
-4000
Differential Capacity [mAh g-1/V]
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
Electrode Potential [V vs. Li]

FIGURE 1B

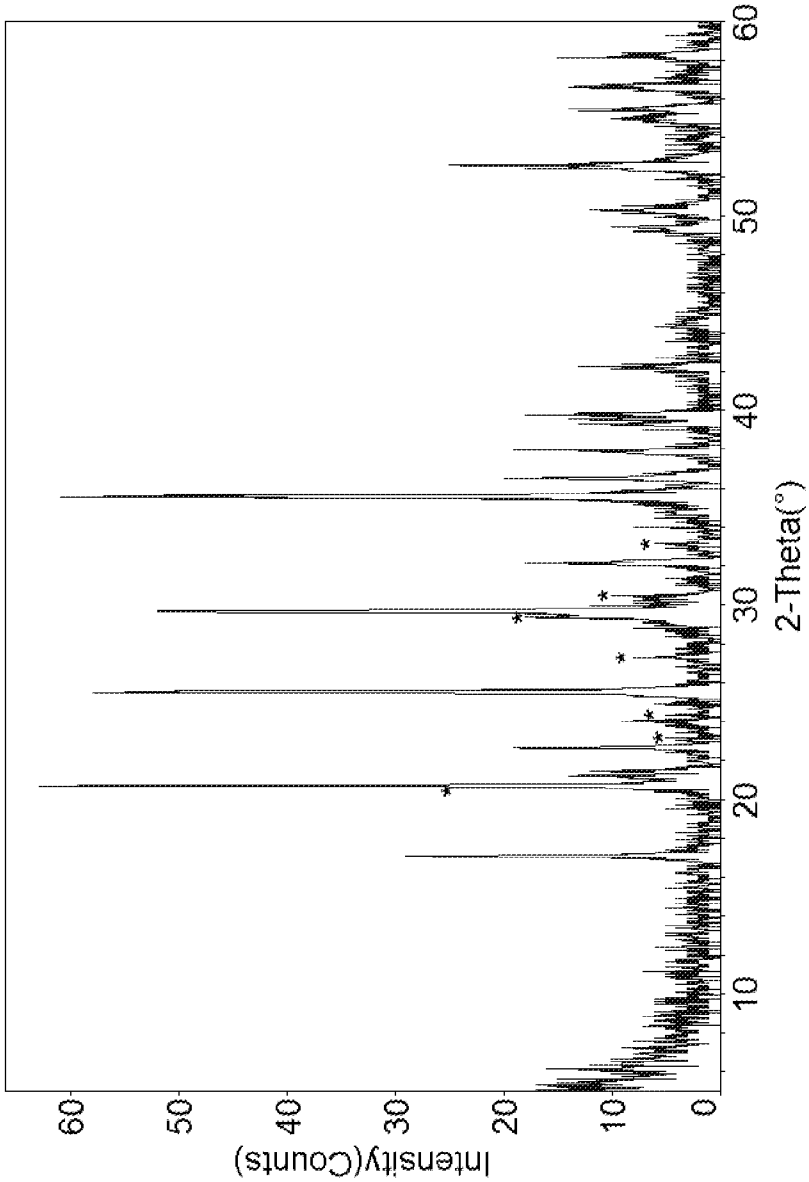

FIGURE 1C

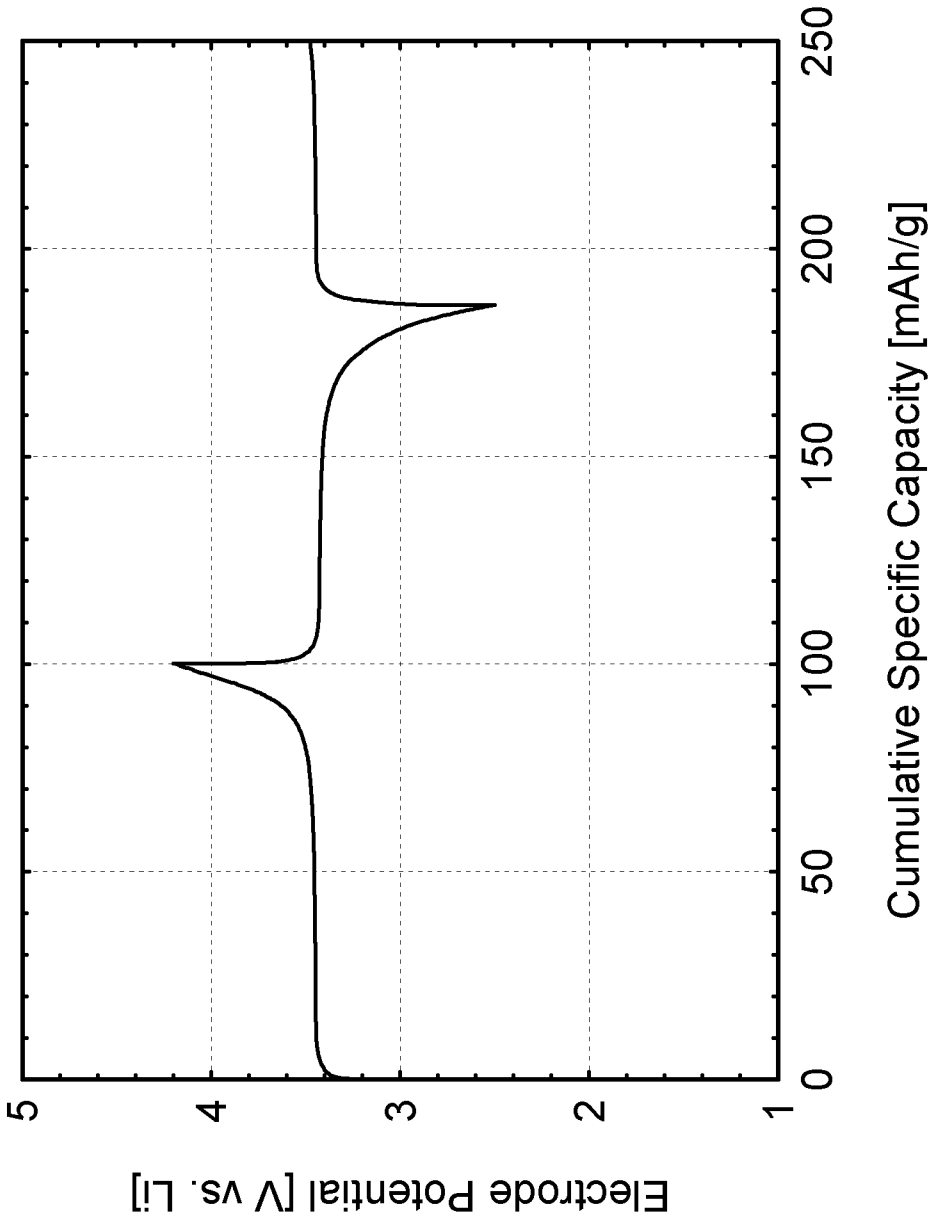
Electrode Potential [V vs. Li]
5
4
3
2
1
0
50
100
150
200
250
Cumulative Specific Capacity [mAh/g]

FIGURE 2A

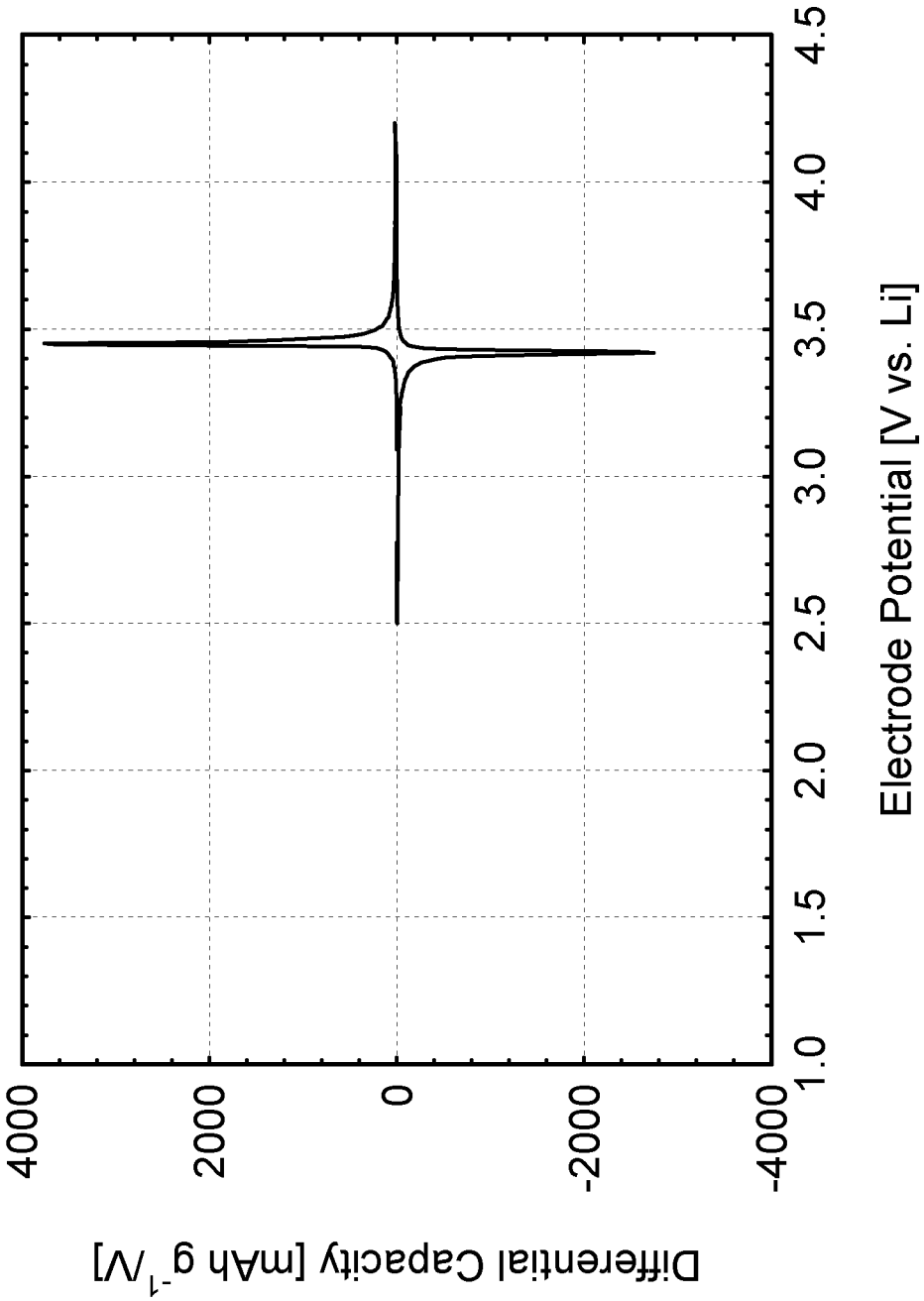
Differential Capacity [mAh g-1/V]
4000
2000
0
-2000
-4000
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
Electrode Potential [V vs. Li]

FIGURE 2B

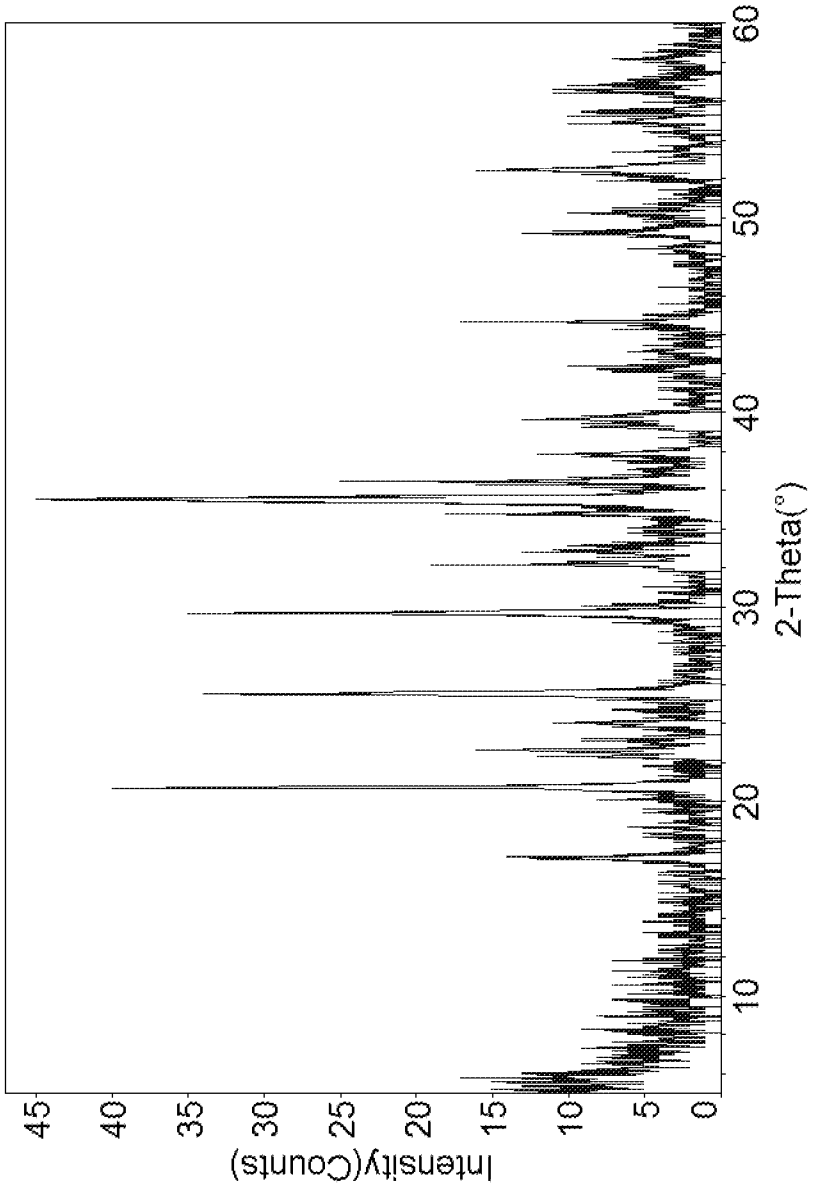
Intensity(Counts)
0
5
10
15
20
25
30
35
40
45
10
20
30
40
50
60
2-Theta(°)

FIGURE 2C

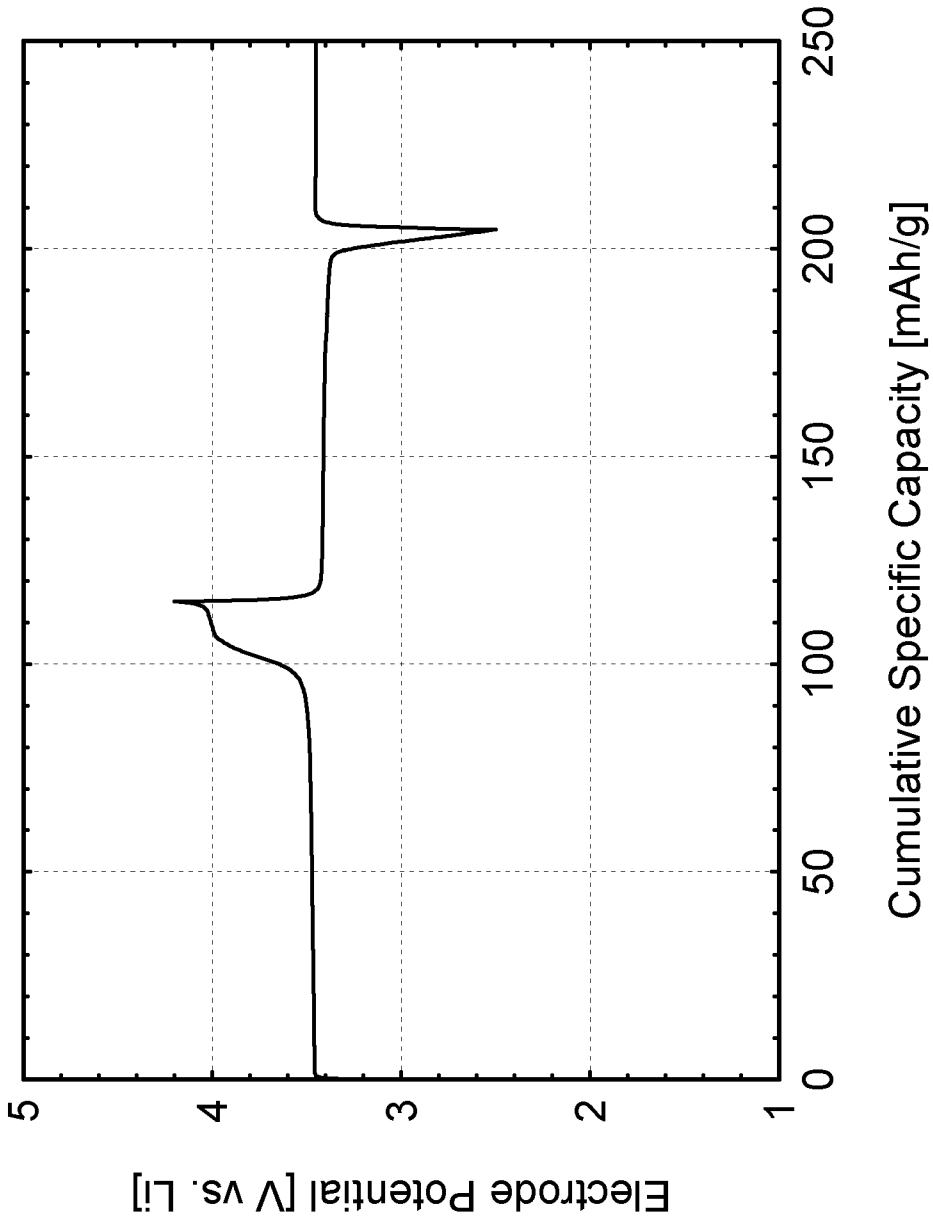
Electrode Potential [V vs. Li]
5
4
3
2
1
0
50
100
150
200
250
Cumulative Specific Capacity [mAh/g]

FIGURE 3A

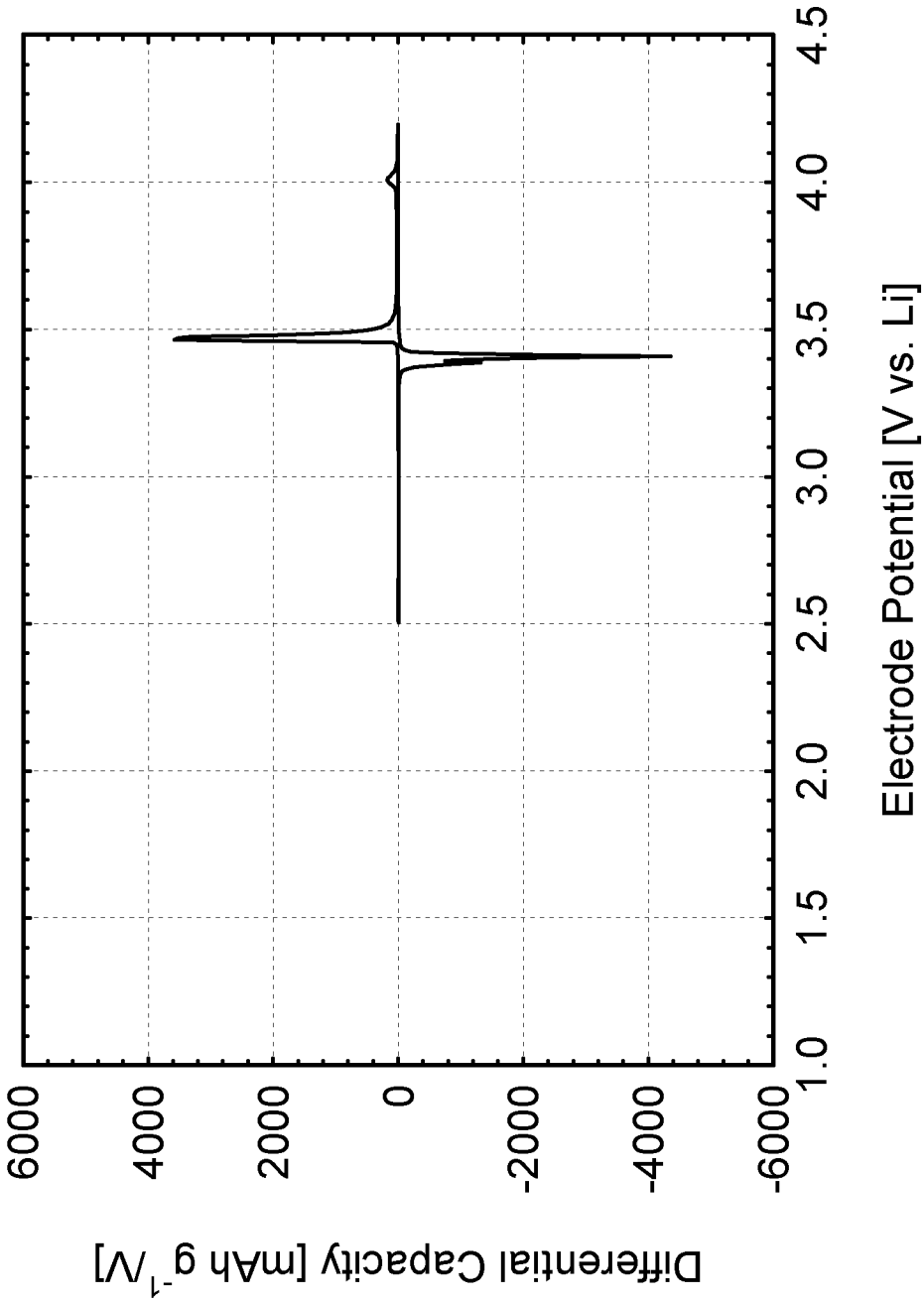
Differential Capacity [mAh g-1/V]
6000
4000
2000
0
-2000
-4000
-6000
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
Electrode Potential [V vs. Li]

FIGURE 3B

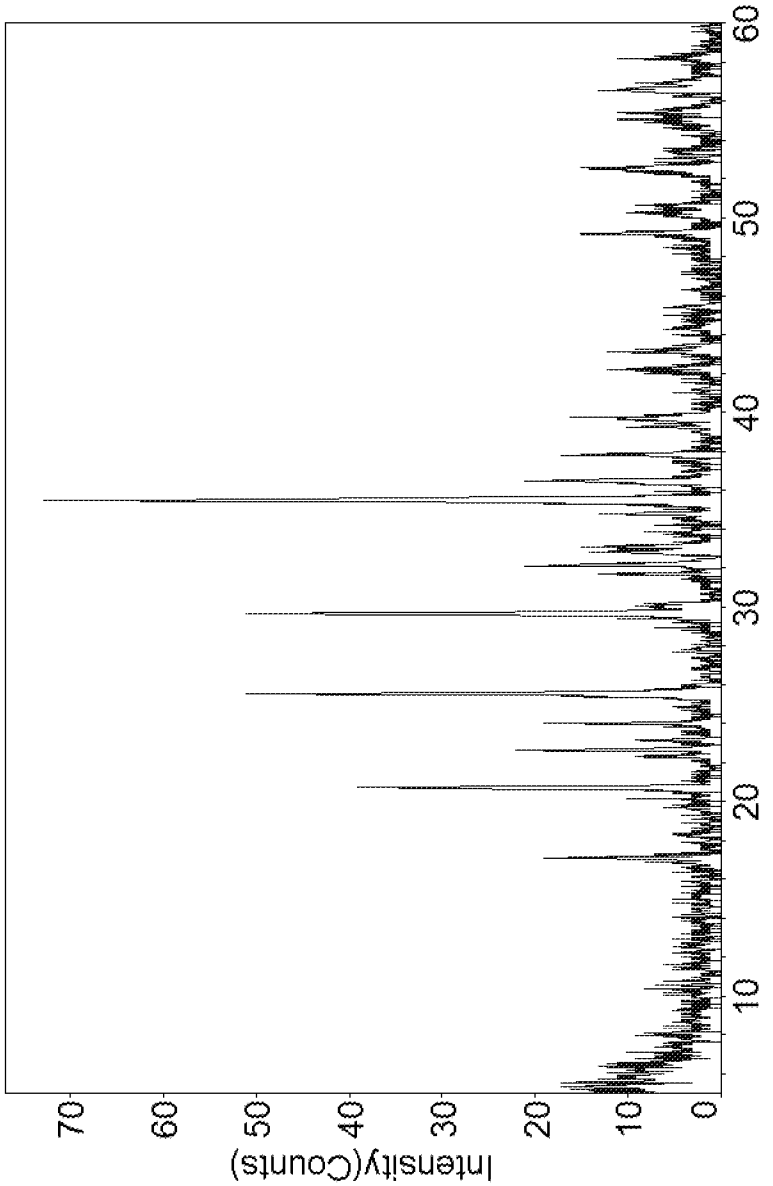

FIGURE 3C

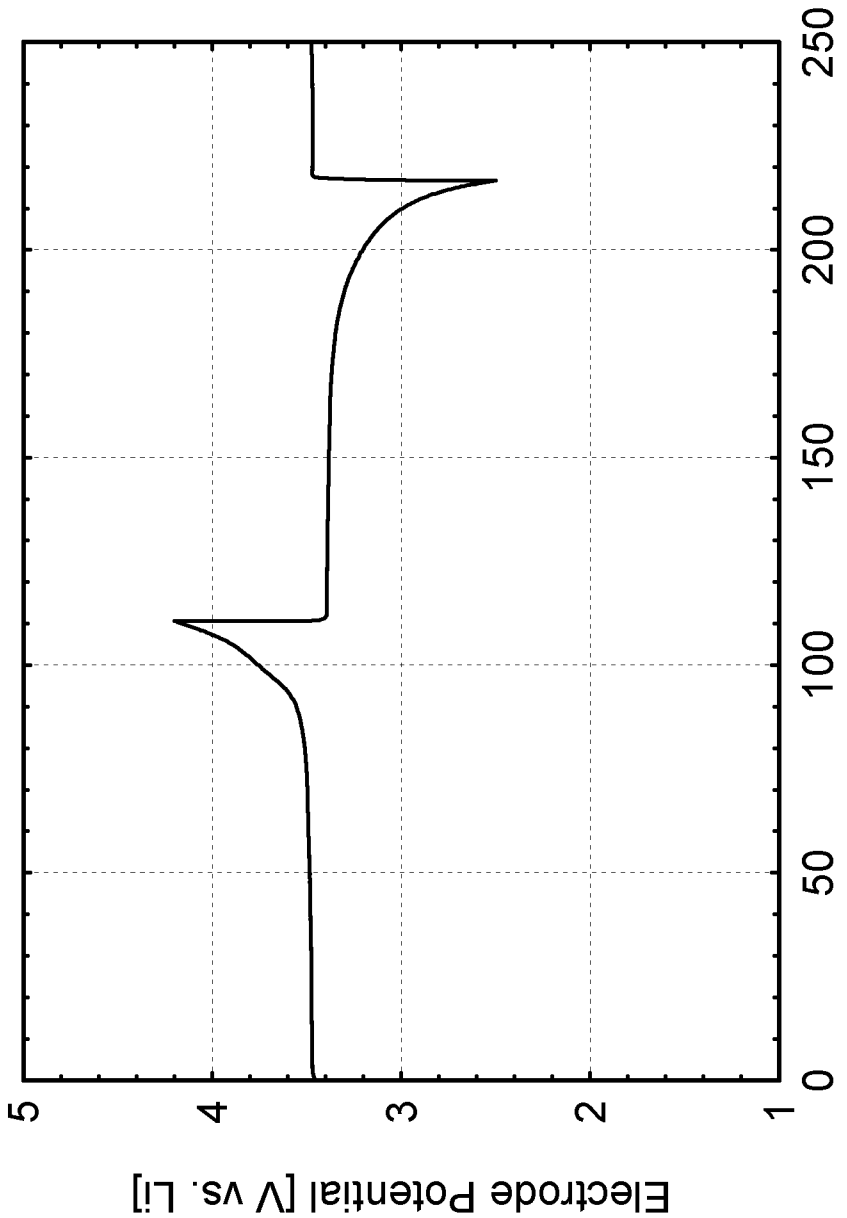
Electrode Potential [V vs. Li]
5
4
3
2
1
0
50
100
150
200
250
Cumulative Specific Capacity [mAh/g]

FIGURE 4A

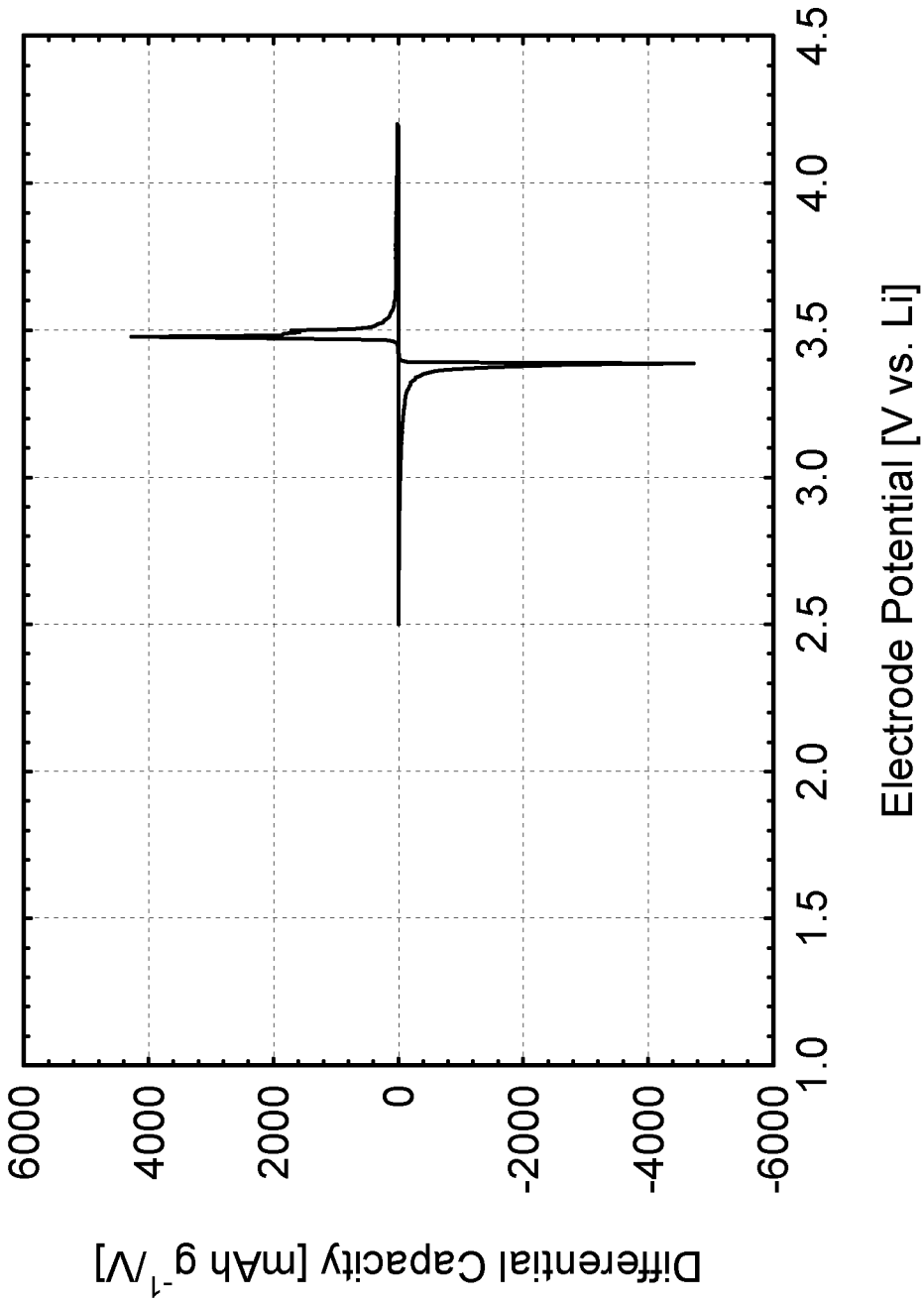
Differential Capacity [mAh g-1/V]
6000
4000
2000
0
-2000
-4000
-6000
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
Electrode Potential [V vs. Li]

FIGURE 4B

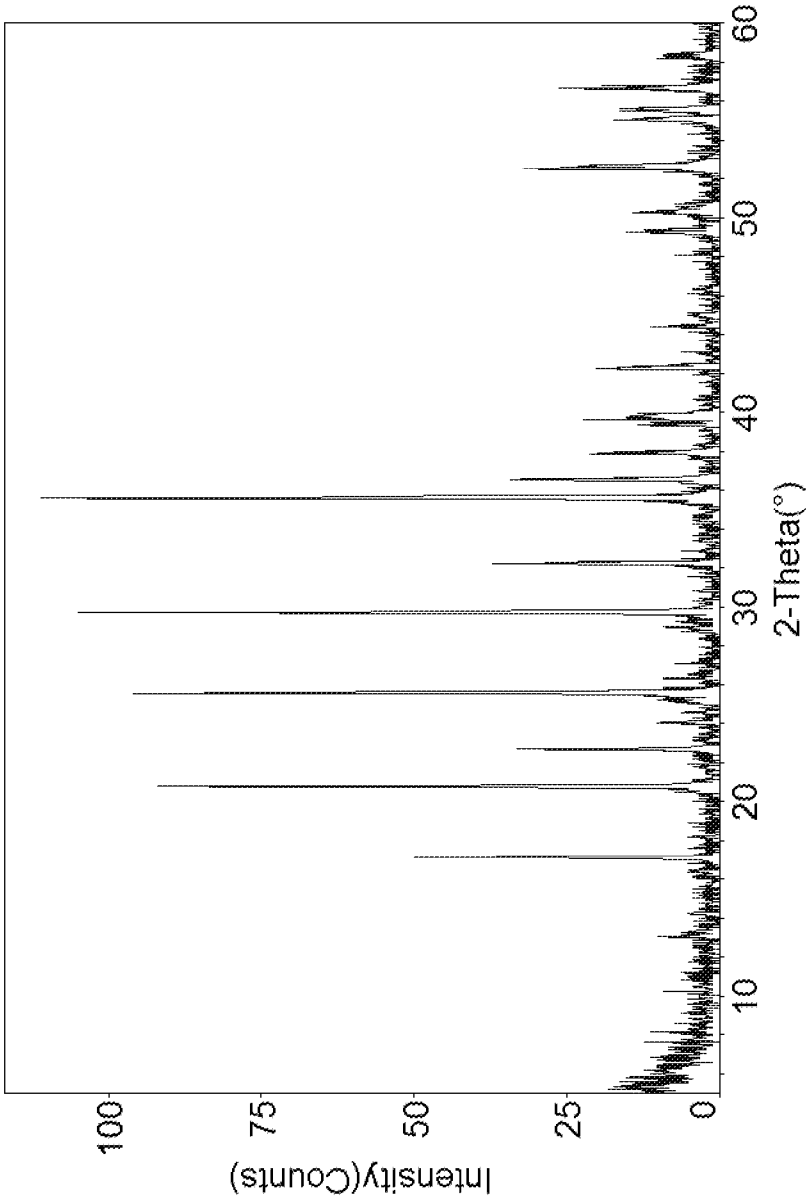

FIGURE 4C

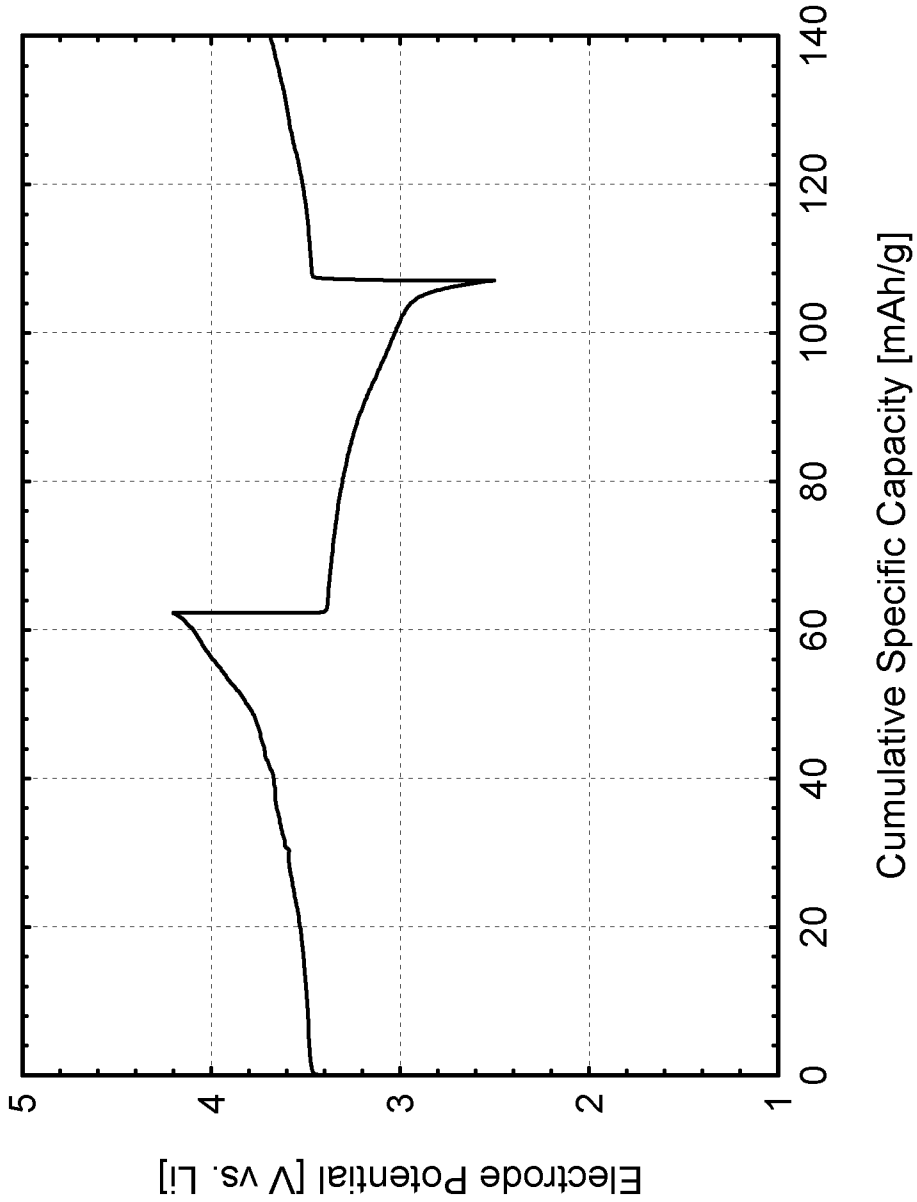
Electrode Potential [V vs. Li]
5
4
3
2
1
0
20
40
60
80
100
120
140
Cumulative Specific Capacity [mAh/g]

FIGURE 5A

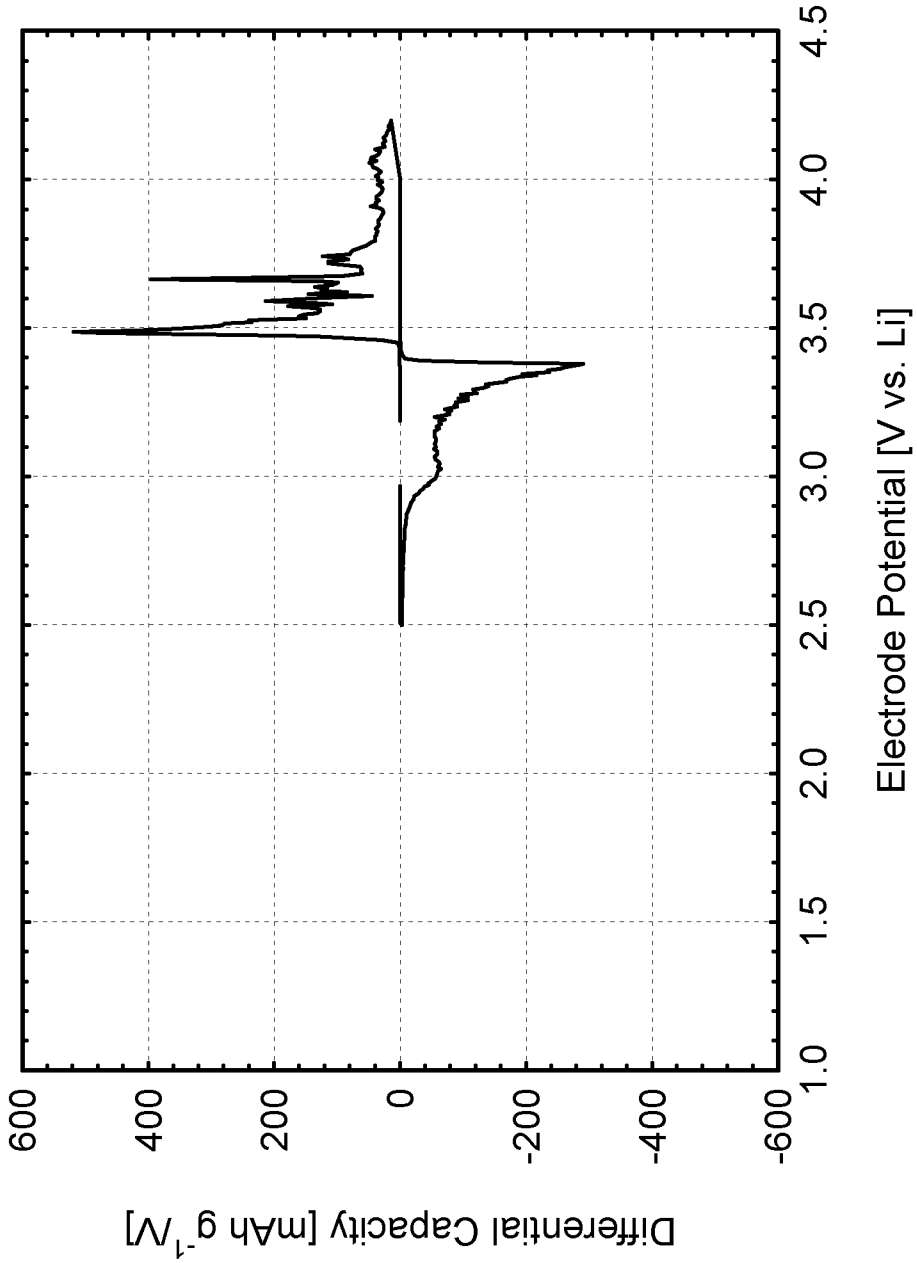
Differential Capacity [mAh g-1/V]
600
400
200
0
-200
-400
-600
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
Electrode Potential [V vs. Li]

FIGURE 5B

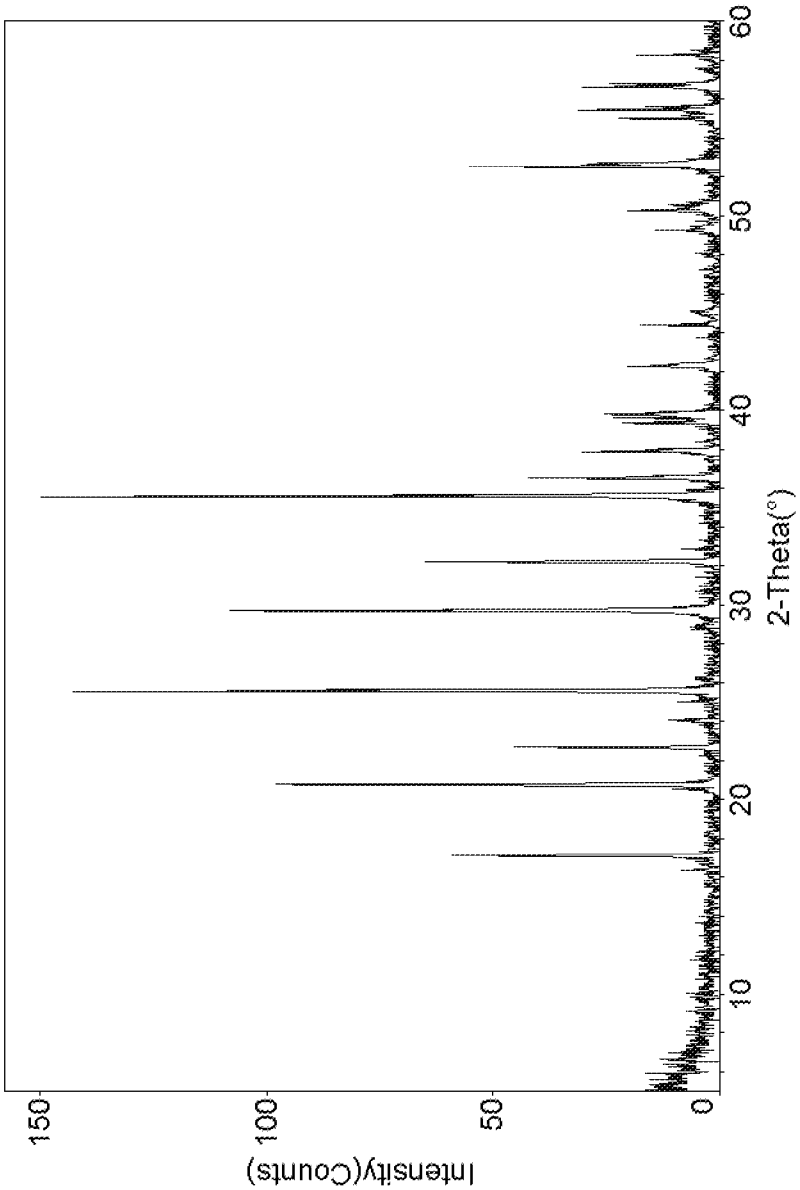

FIGURE 5C

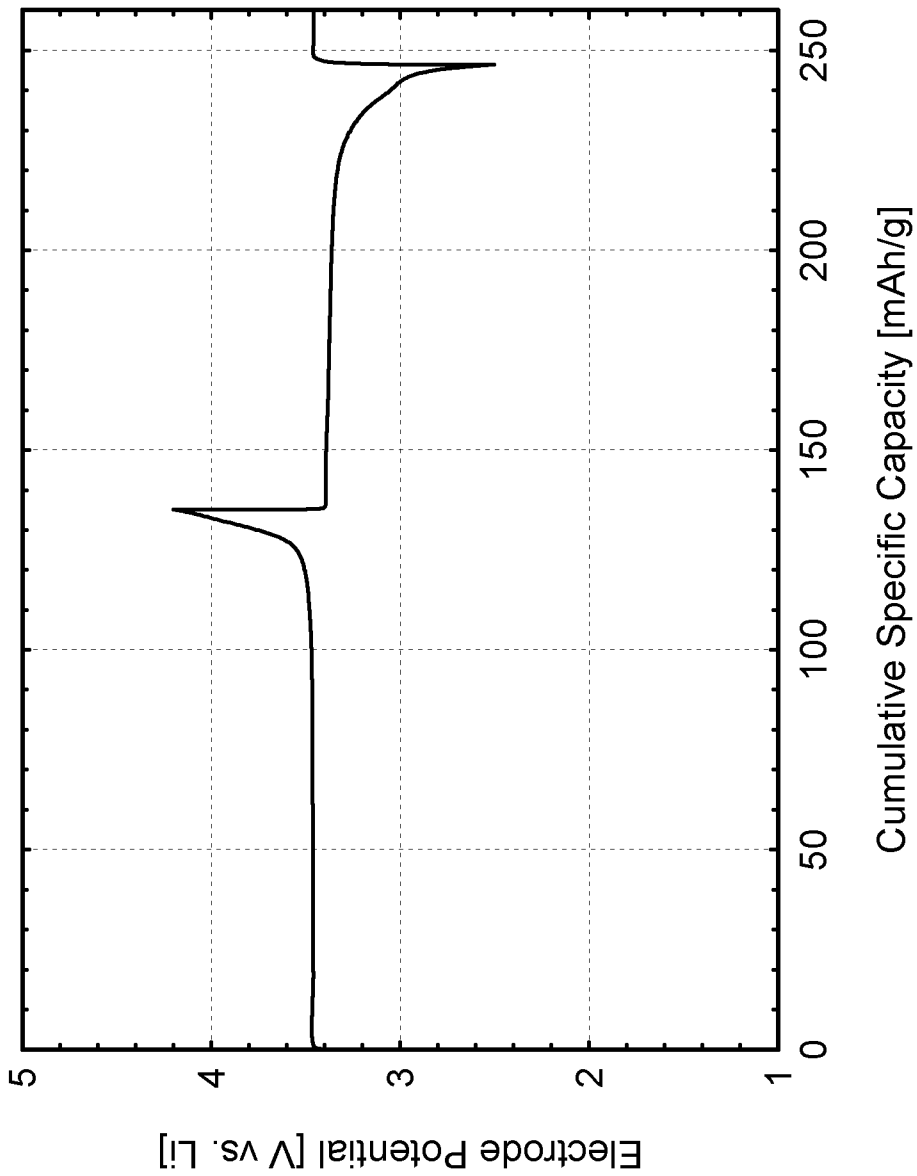
Electrode Potential [V vs. Li]
5
4
3
2
1
0
50
100
150
200
250
Cumulative Specific Capacity [mAh/g]

FIGURE 6A

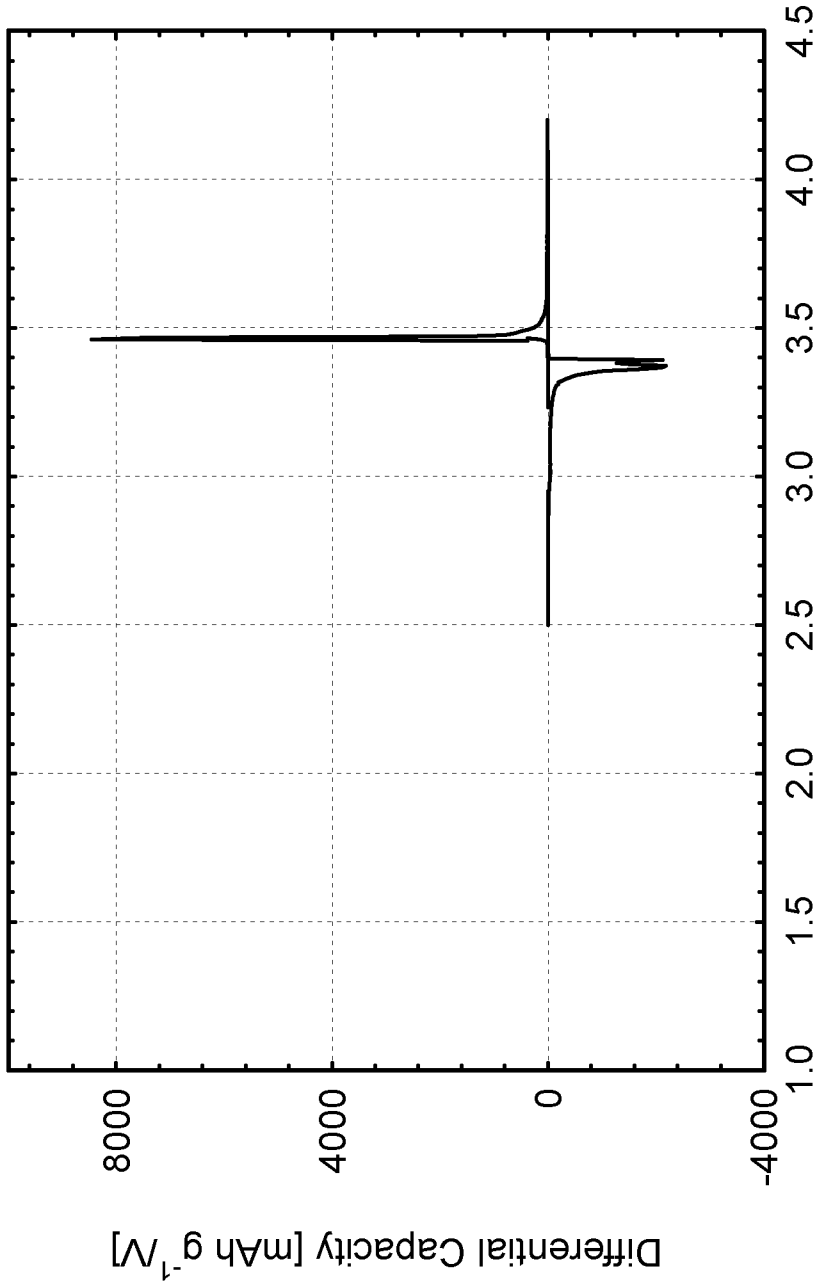
Differential Capacity [mAh g-1/V]
8000
4000
0
-4000
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
Electrode Potential [V vs. Li]

FIGURE 6B

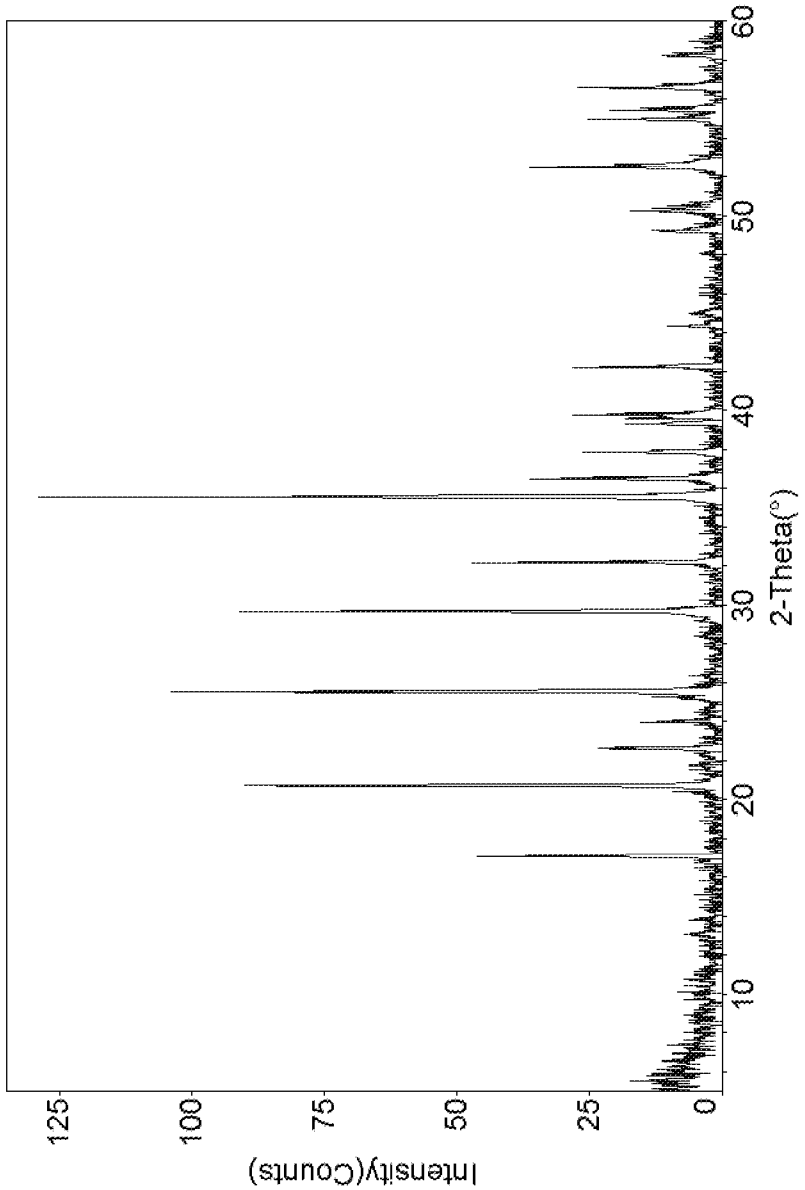

FIGURE 6C

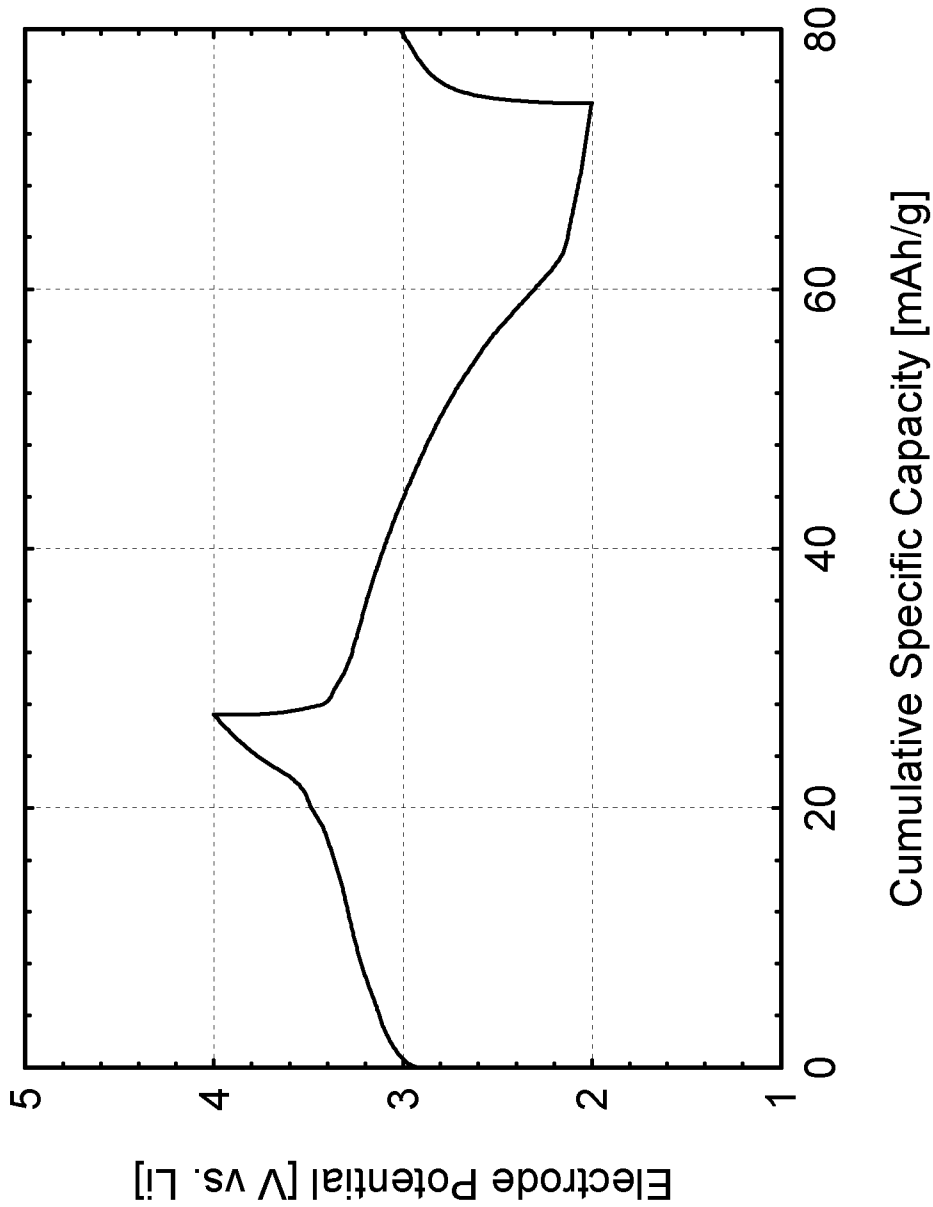
Electrode Potential [V vs. Li]
5
4
3
2
1
0
20
40
60
80
Cumulative Specific Capacity [mAh/g]

FIGURE 7A

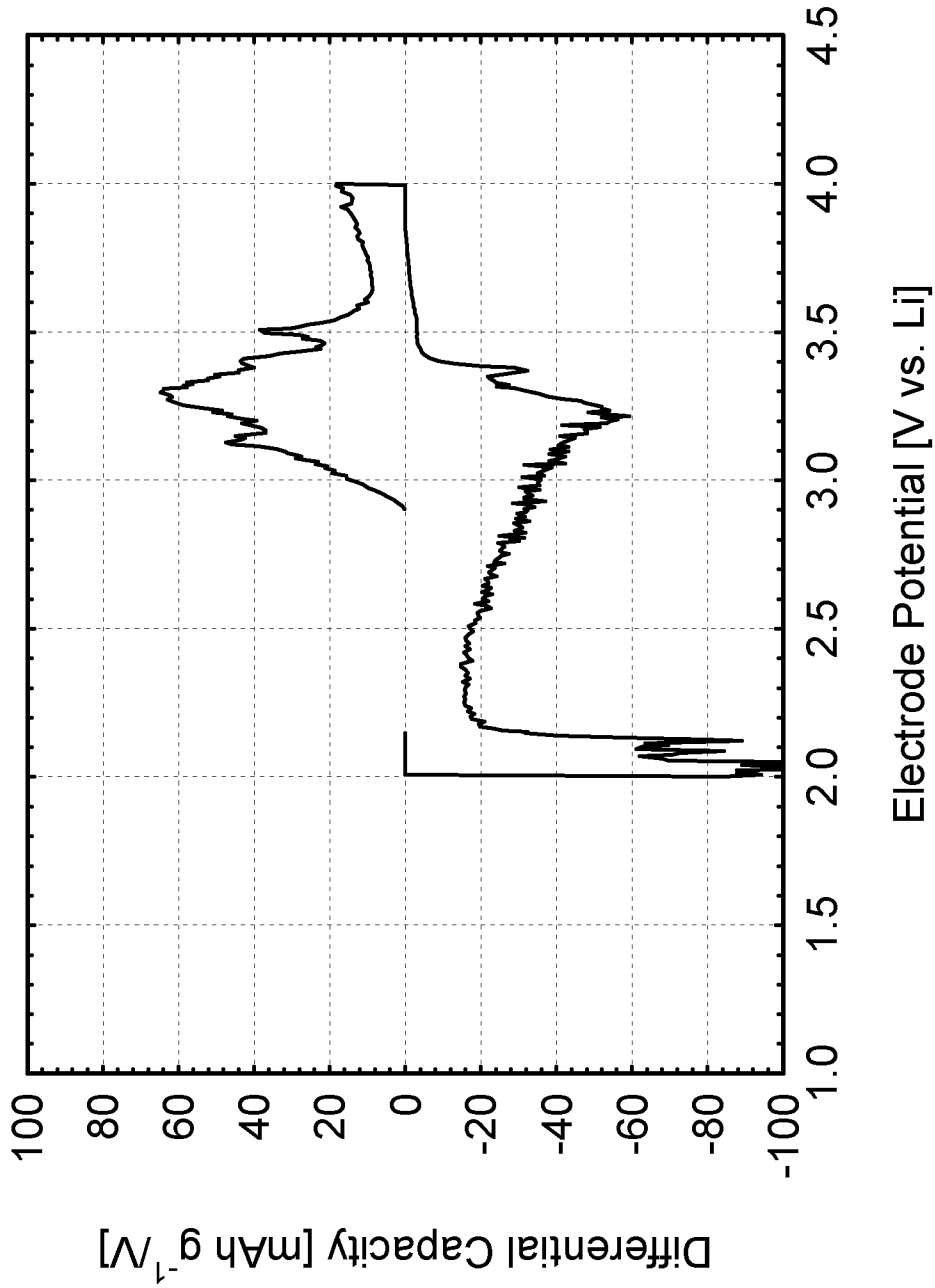
Differential Capacity [mAh g-1/V]
100
80
60
40
20
0
-20
-40
-60
-80
-100
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
Electrode Potential [V vs. Li]

FIGURE 7B

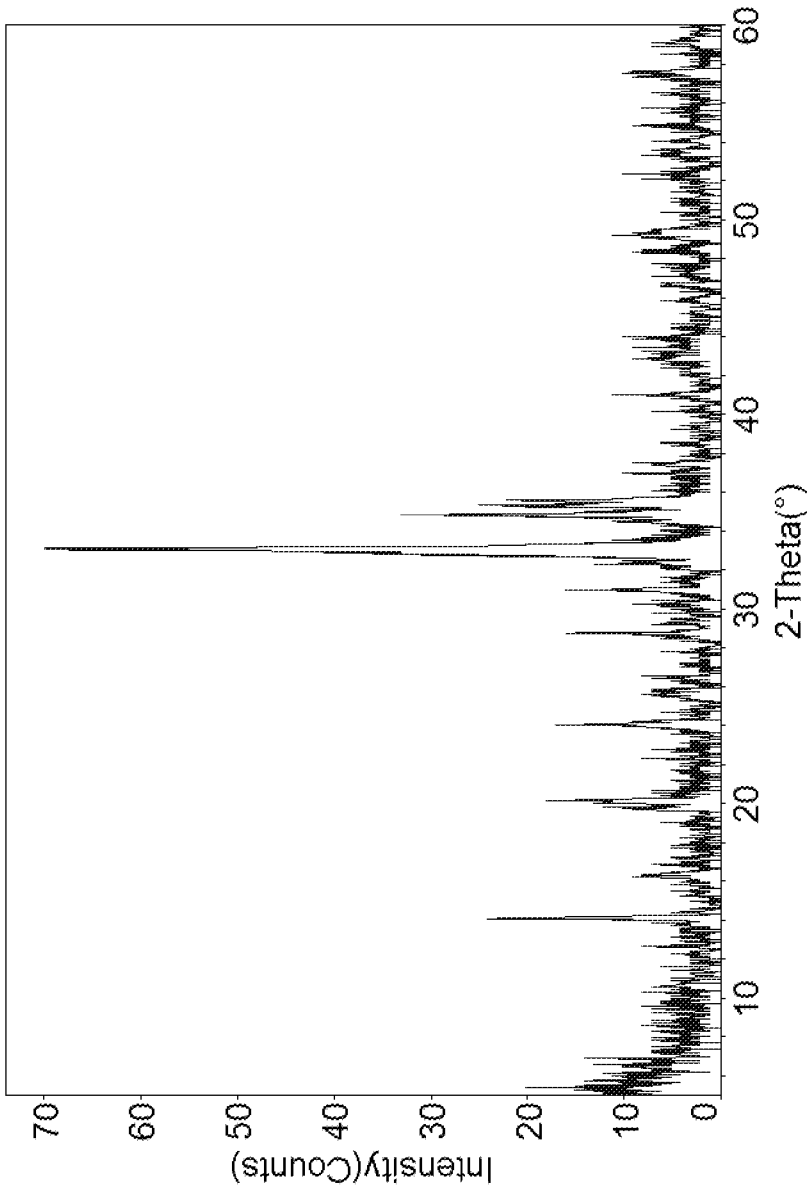

FIGURE 7C

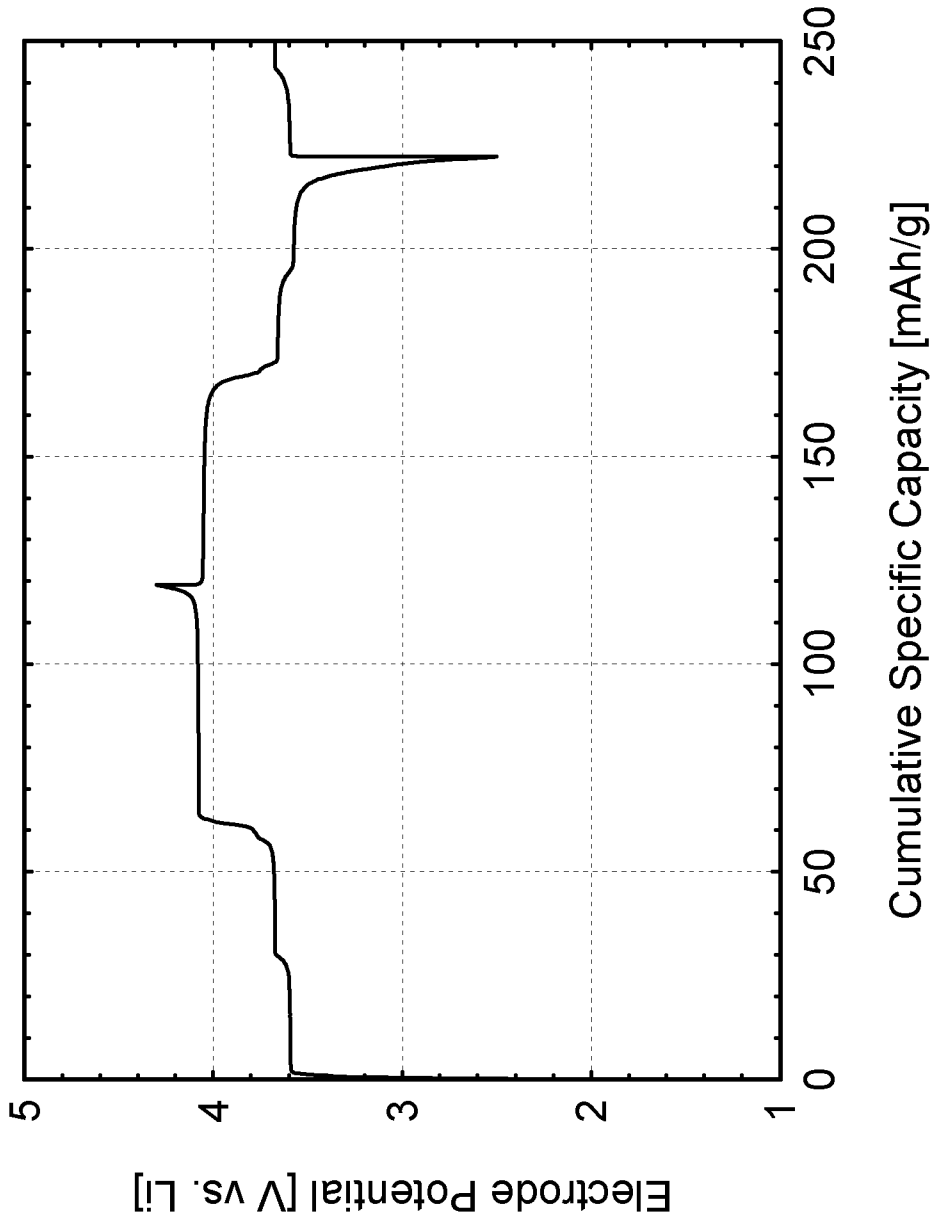
Electrode Potential [V vs. Li]
5
4
3
2
1
0
50
100
150
200
250
Cumulative Specific Capacity [mAh/g]

FIGURE 8A

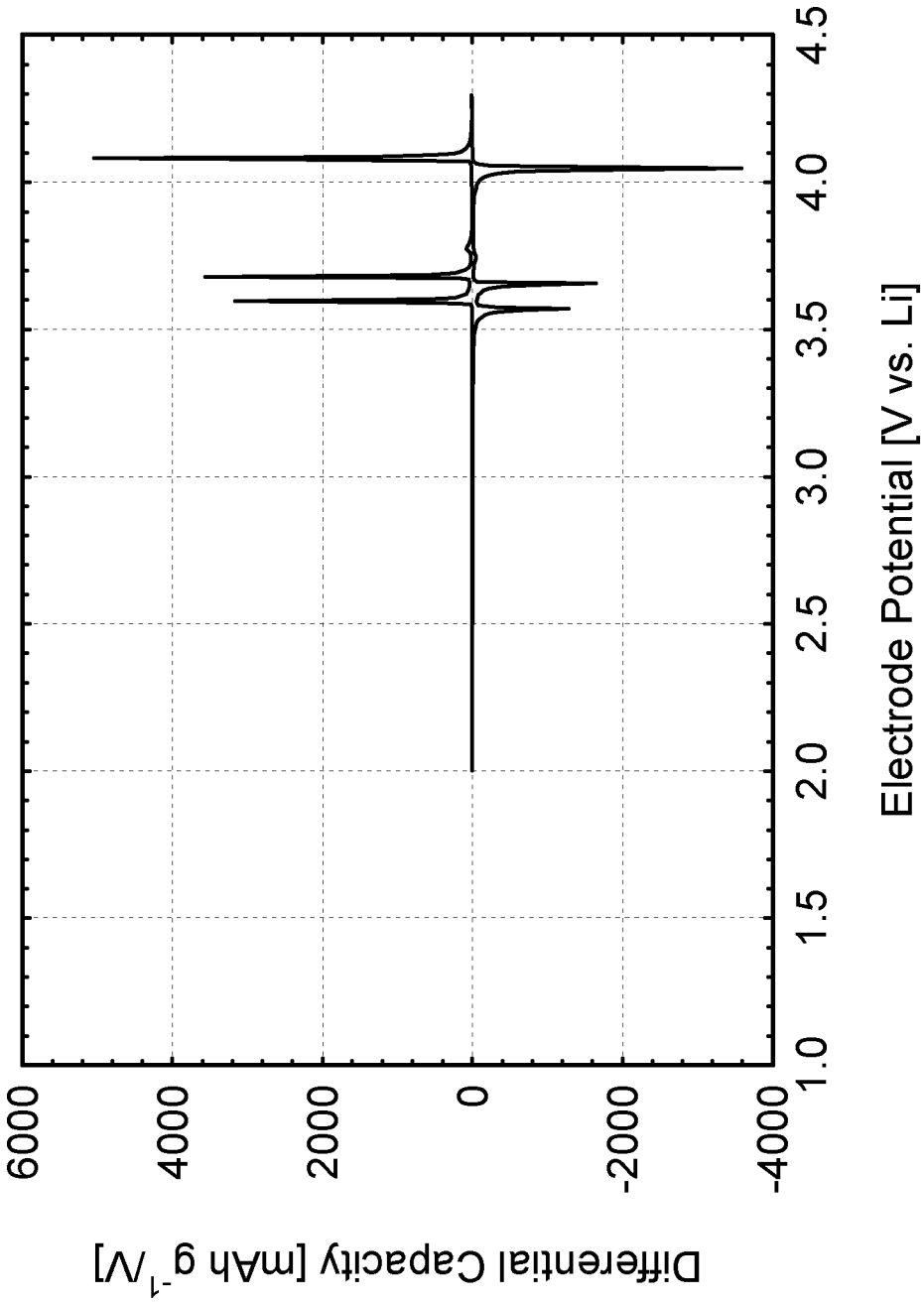
Differential Capacity [mAh g-1/V]
6000
4000
2000
0
-2000
-4000
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
Electrode Potential [V vs. Li]

FIGURE 8B

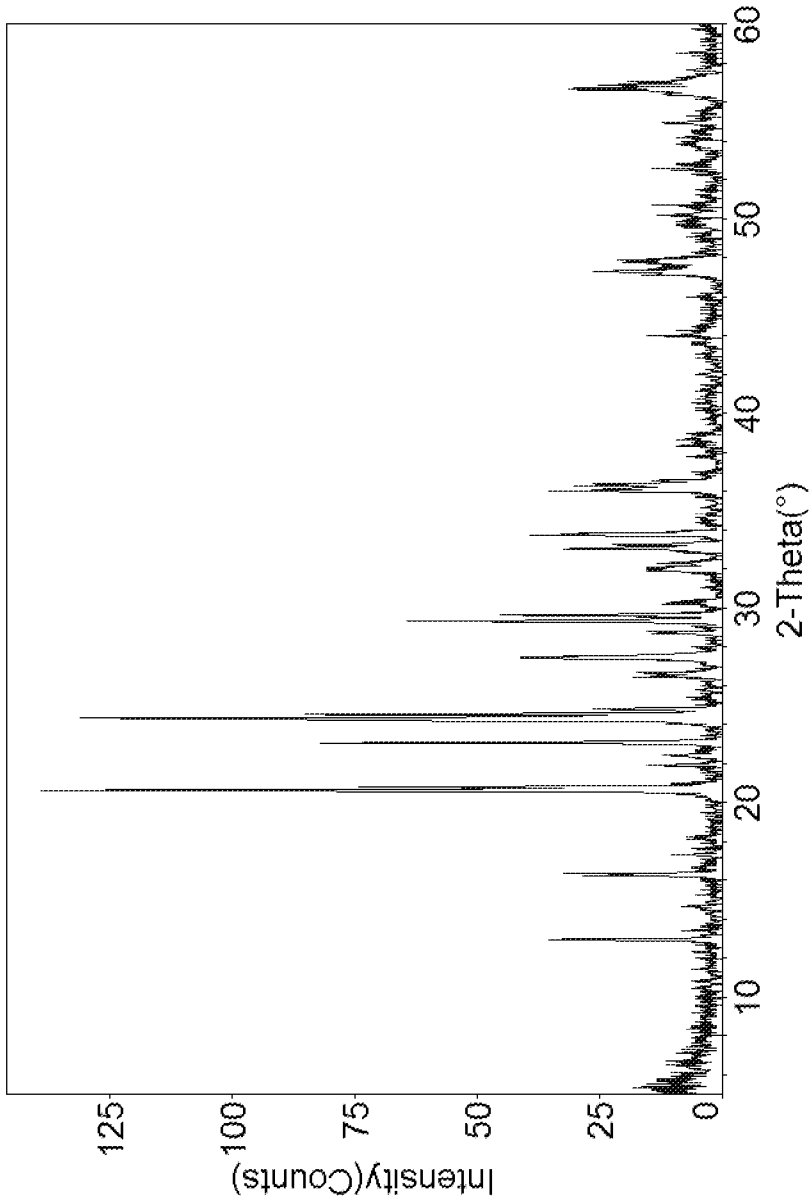

FIGURE 8C

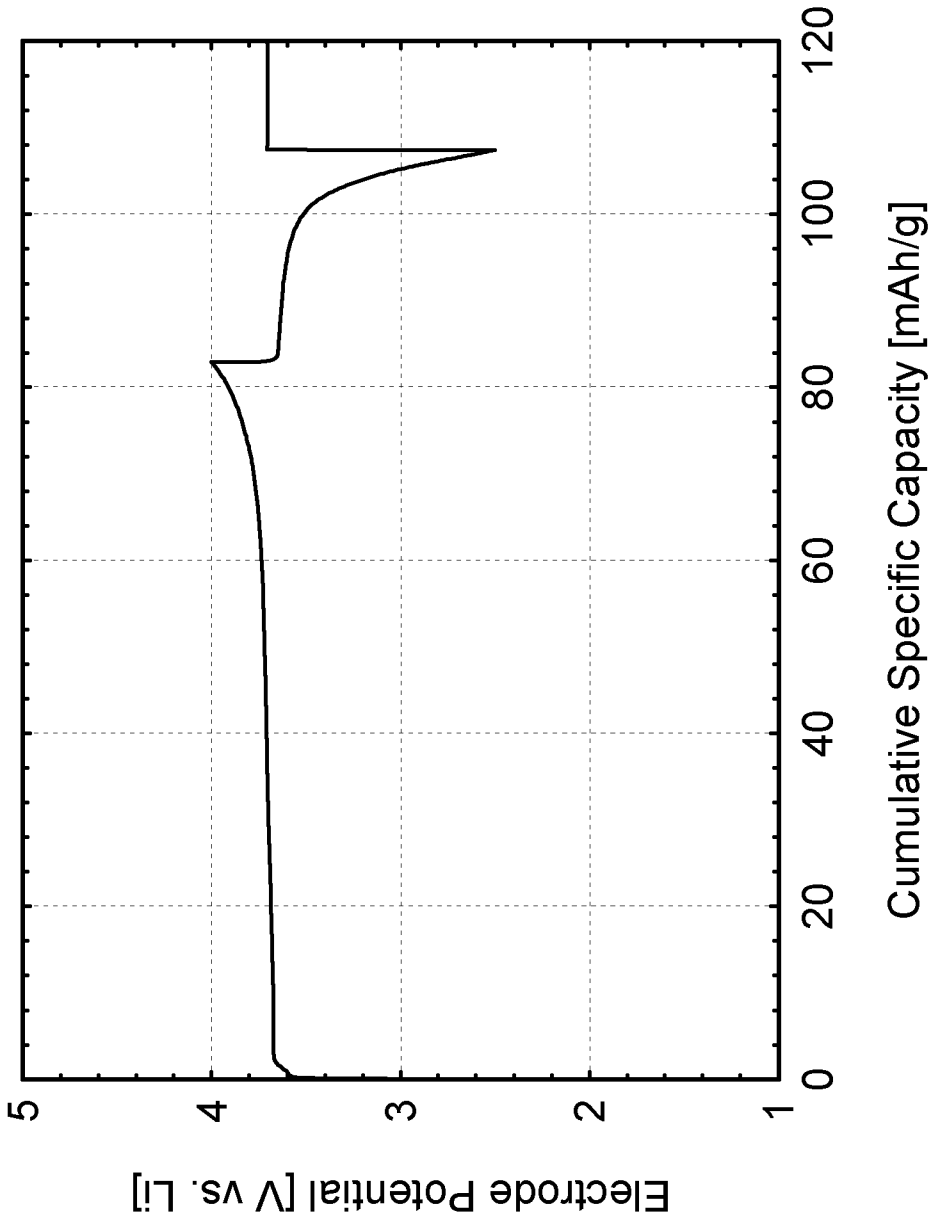
Electrode Potential [V vs. Li]
5
4
3
2
1
0
20
40
60
80
100
120
Cumulative Specific Capacity [mAh/g]

FIGURE 9A

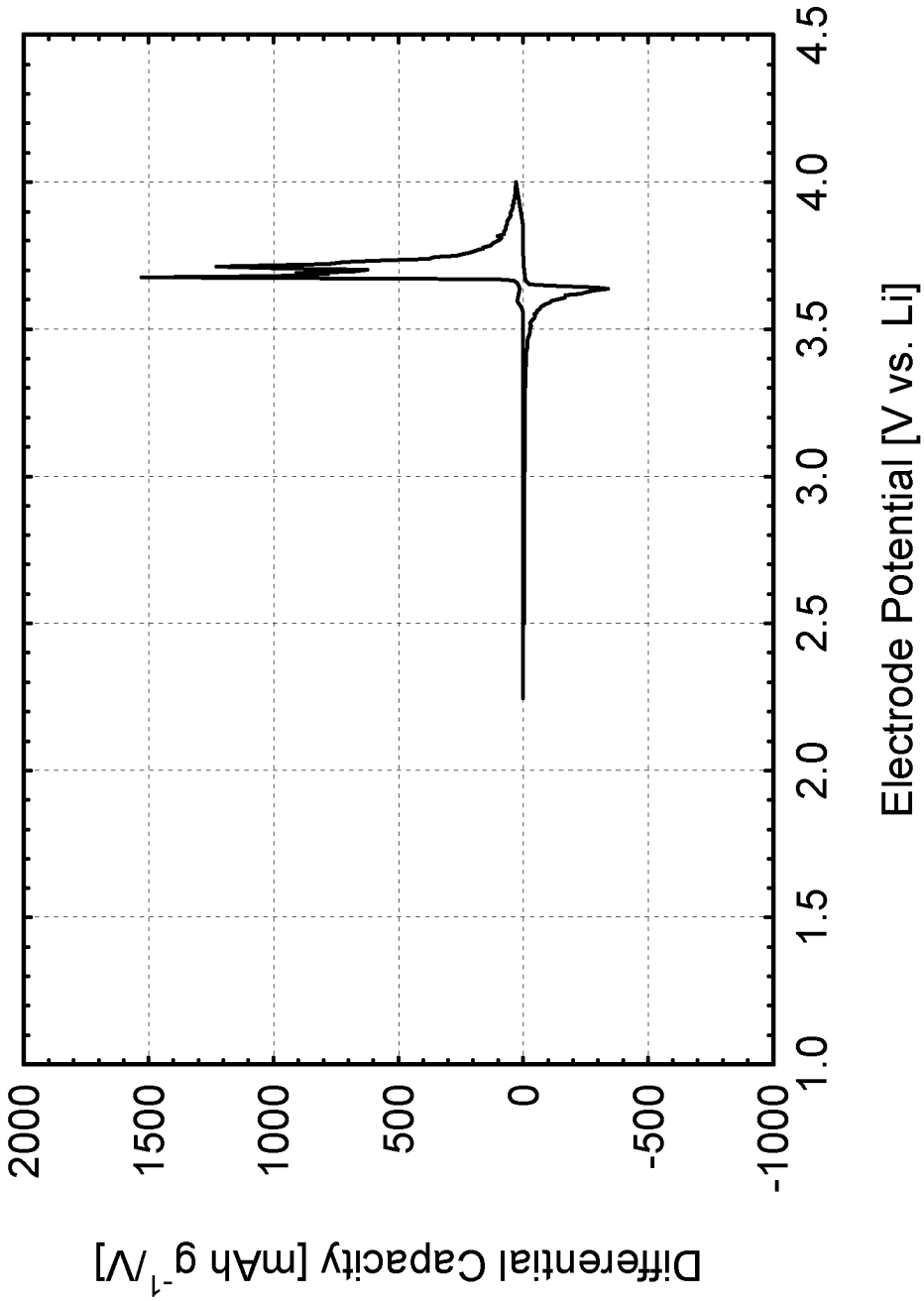
Differential Capacity [mAh g-1/V]
2000
1500
1000
500
0
-500
-1000
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
Electrode Potential [V vs. Li]

FIGURE 9B

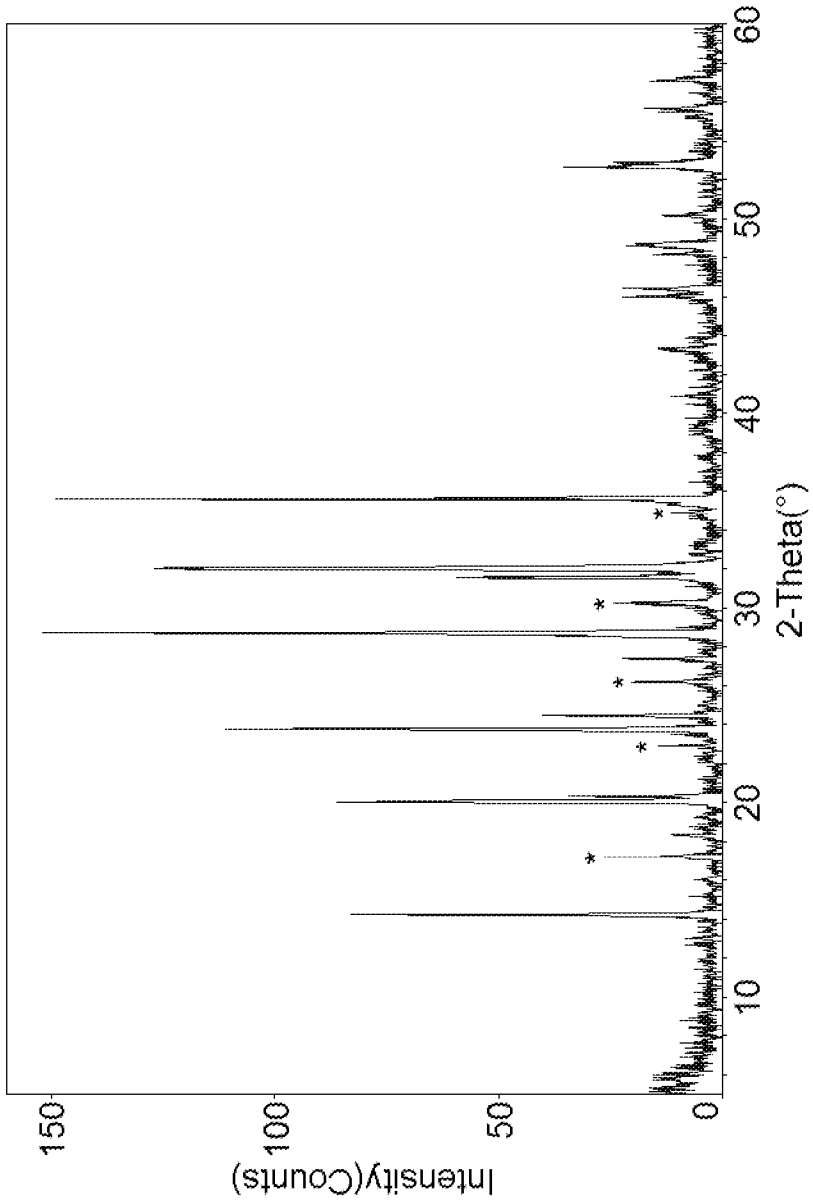

FIGURE 9C

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2014/051456

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B25/30 C01B25/37 C01B25/45 H01M4/58
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)
C01B 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, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2003/027049 A1 (BARKER JEREMY [GB] ET AL) 6 February 2003 (2003-02-06) examples 1-25	1-17
X	WO 01/53198 A1 (VALENCE TECHNOLOGY INC [US]; BARKER JEREMY [GB]; SAIDI M YAZID [US]; S) 26 July 2001 (2001-07-26) claims 1-30; figures 1/23-23/23; examples 1-10	1-17
X	US 2007/134554 A1 (ARMAND MICHEL [CA] ET AL) 14 June 2007 (2007-06-14) See all examples;	1-17

☐ 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	Date of mailing of the international search report
1 August 2014	11/08/2014

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Fortunati, Taddiano

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2014/051456

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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