



(51) International Patent Classification:

C01D 15/04 (2006.01) **C22B 3/20** (2006.01)
C22B 26/12 (2006.01)

(21) International Application Number:

PCT/AU2017/050100

(22) International Filing Date:

08 February 2017 (08.02.2017)

(25) Filing Language:

English

(26) Publication Language:

English

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

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,

(54) Title: COMBINED PROCESSING METHOD INCORPORATING ELECTROLYSIS FOR LITHIUM CONTAINING SOLUTIONS

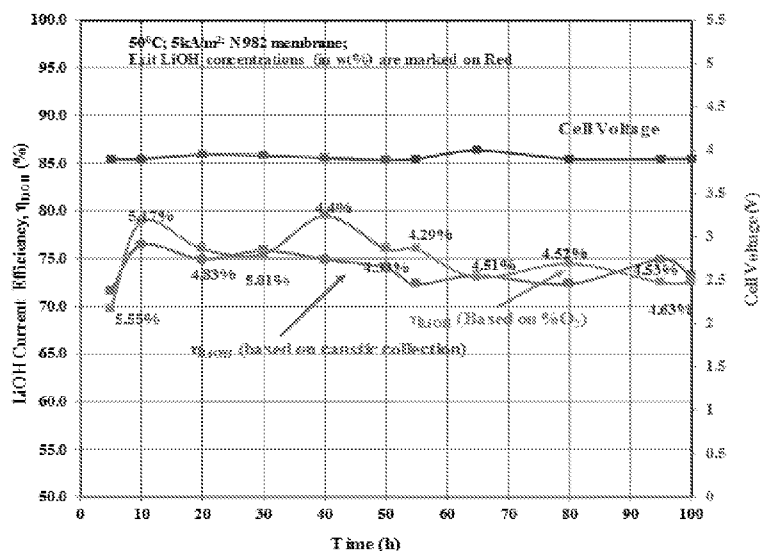


Figure 52

(57) Abstract: A combined processing method for the purification of lithium containing solutions, the method comprising the method steps of: a) passing a lithium containing solution to one or more purification steps to produce a substantially purified lithium chloride solution; and b) passing the substantially purified lithium chloride solution of step a) to an electrolysis step in which lithium hydroxide monohydrate is produced, wherein the one or more purification steps comprises either or both of a first purification step in which the lithium containing solution is contacted with a titanate adsorbent whereby lithium ions are adsorbed thereon whilst rejecting substantially all other cations, the recovery of lithium from the adsorbent providing a part-purified lithium containing solution, and a second purification step in which a graphene based filter medium is utilised to provide a further purified lithium containing solution.



TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
KM, ML, MR, NE, SN, TD, TG).

Published:

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

“Combined Processing Method Incorporating Electrolysis for Lithium Containing Solutions”

Field of the Invention

[0001] The present invention relates to a combined processing method incorporating electrolysis for lithium containing solutions.

[0002] More particularly, the method of the present invention is intended for use in the extraction of lithium chloride from a lithium containing brine. In one form the extraction of lithium chloride from a lithium containing brine is achieved through the combined action of an adsorbent and/or a filter utilising a graphene based filter medium, with an electrolysis step.

[0003] Still more particularly, the adsorbent is derived from titanium dioxide, and in the form of either sodium titanate ($\text{Na}_2\text{Ti}_3\text{O}_7$) or hydrogen titanate (H_2TiO_3).

[0004] The present invention still further relates to a process for the purification of a lithium chloride solution obtained through either adsorption of lithium on an adsorbent, such as sodium titanate or hydrogen titanate, and/or filtration using a graphene based filter medium, combined with an electrolysis step, to prepare high purity lithium chloride solution for use in battery applications. This is particularly achieved through a process in which a semi-pure or partially purified lithium chloride solution obtained through either desorption on an adsorbent and/or filtration using a graphene based membrane is passed to an electrolysis step.

[0005] The graphene based filter medium employed in the process of the present invention is particularly, in one form, graphene oxide (GO) or reduced graphene oxide (rGO). It is envisaged that the graphene based filter medium acts as an ion sieve, allowing ions with smaller sizes than those of the channels to permeate while blocking all other larger species. In this manner it is understood that the graphene based filter medium rejects impurities such as K, Na and Mg, allowing the purification of a LiCl containing solution.

[0006] Yet still more particularly, the electrolysis step is intended to provide a lithium hydroxide monohydrate product.

Background Art

[0007] Lithium salts have widespread commercial application. They are used in the production of lithium metal, lithium carbonate and lithium hydroxide monohydrate for various battery applications. Due to the requirement for high purity in many of these applications, particularly when used as a cathode material in lithium ion batteries, there is an ever increasing need for high purity lithium chloride.

[0008] Traditionally, lithium chloride from a brine source is purified by solar evaporation technology to concentrate the brine solution and thereby remove sodium and potassium impurities. Other impurities, such as boron, may be removed by solvent extraction technology, whereas calcium, magnesium and other similar impurities may be removed by increasing the pH of the brine solution. This is typically achieved through the addition of lime and the formation and precipitation of insoluble salts, including calcium carbonate. This is very time consuming and highly dependent on the weather. Therefore, a purification means is needed to remove the majority of the impurities from a LiCl solution derived from a brine source, such that the concentration of each impurity is reduced to less than about 20 ppm.

[0009] An impurity concentration of less than about 20 ppm makes the resulting LiCl solution suitable for use in lithium metal extraction or the preparation of other lithium compounds, including lithium carbonate and lithium hydroxide monohydrate, for use in lithium ion battery applications.

[0010] The processes of the present invention have as one object thereof to overcome substantially one or more of the above mentioned problems associated with prior art, or to at least provide a useful alternative thereto.

[0011] The preceding discussion of the background art is intended to facilitate an understanding of the present invention only. This discussion is not an acknowledgement or admission that any of the material referred to is or was part of the common general knowledge as at the priority date of the application.

[0012] Throughout the specification and claims, unless the context requires otherwise, the word “comprise” or variations such as “comprises” or “comprising”, will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

[0013] The term brine, or brines, or variations thereof, is to be understood to include a solution of alkali and/or alkaline earth metal salt(s) in water, of a natural or possibly industrial source. The concentrations of the various salts can vary widely. The ions present in brine may include a combination of one or more of a monovalent cation, such as lithium, multivalent cations, monovalent anions, and multivalent anions.

[0014] The term high purity lithium chloride is to be understood, unless the context requires otherwise, as requiring any impurity present to be present in amounts of less than about 20 ppm.

[0015] The term graphene, graphene sheet or graphene material is to be understood, unless the context requires otherwise, as including single layer graphene, few layer graphene (FLG), graphene nano-platelets, graphene nanotubes, graphene nanoribbons, graphene nano-sheets and the like.

Disclosure of the Invention

[0016] In accordance with the present invention there is provided a combined processing method for the purification of lithium containing solutions, the method comprising the method steps of:

- a) passing a lithium containing solution to one or more purification steps to produce a substantially purified lithium chloride solution; and
- b) passing the substantially purified lithium chloride solution of step a) to an electrolysis step in which a lithium hydroxide product is produced,

wherein the one or more purification steps comprises either or both of a first purification step in which the lithium containing solution is contacted with a titanate adsorbent whereby lithium ions are adsorbed thereon whilst rejecting substantially all other

cations, the recovery of the lithium from the adsorbent providing a part-purified lithium containing solution, and a second purification step in which a graphene based filter medium is utilised to provide a further purified lithium containing solution.

[0017] In one form, the lithium containing solution is a lithium containing brine.

[0018] Preferably, the part-purified lithium containing solution produced in the first purification step is passed in whole or part to the second purification step.

[0019] Preferably, the adsorbent is provided in the form of either a hydrated titanium dioxide or a sodium titanate. In one form of the present invention the hydrated titanium dioxide is produced from titanium dioxide.

[0020] Still preferably, the process in turn produces a substantially pure lithium chloride solution.

[0021] The brine preferably contains impurities from the group of sodium, potassium, magnesium, calcium and borate.

[0022] Still preferably, the impurity concentration of the substantially pure lithium chloride solution does not exceed about 20 ppm.

[0023] In one form of the present invention the brine contains lithium in the range of about 500 to 1500 ppm, and impurities including magnesium in the range of about 0.15% to 0.30%, calcium in the range of about 0.05% to 0.1%, sodium in the range of about 8 to 10%, potassium in the range of about 0.7% to 1.0%, and borate in the range of about 0.15% to 0.20%.

[0024] In a more preferred form of the present invention, the brine contains about 700 ppm lithium, about 0.19% magnesium, about 0.09% calcium, about 8.8% sodium, about 0.8% potassium and about 0.18% borate.

[0025] The brine solution is preferably adjusted to a pH of 7 through the addition of a base. The base is preferably provided in the form of sodium hydroxide.

[0026] The contact between the brine solution and the adsorbent preferably takes place at or about room or ambient temperature.

[0027] In one form of the present invention the brine is collected into a vessel and cooled to room temperature prior to its exposure to the adsorbent. Preferably, room temperature is understood to be between about 20°C to 28°C.

[0028] Preferably, the contact or residence time between the brine solution and the adsorbent is between about 4 to 24 hours.

[0029] Still preferably, the contact or residence time between the brine solution and the adsorbent is:

- a) between about 8 to 24 hours;
- b) between about 20 to 24 hours; or
- c) between about 8 to 16 hours.

[0030] It is to be understood that the contact time is to some extent dependent upon additional variables including reactor size and shape.

[0031] Preferably, the recovery of lithium from the adsorbent is achieved through the regeneration of the adsorbent by the addition of an acid solution and the adsorbed lithium is extracted to provide the part purified lithium containing solution. Still preferably, the acid solution is a solution of hydrochloric acid.

[0032] Still further preferably, the amount of lithium extracted from the adsorbent through exposure to the acid solution is greater than about 90%. Yet still preferably, the amount of lithium extracted from the adsorbent through exposure to the acid solution is about 100% of the adsorbed lithium.

[0033] The graphene based filter medium of the second purification step preferably comprises a graphene membrane formed of one or more graphene, graphene oxide and/or reduced graphene oxide and to which the part-purified lithium containing solution is presented.

[0034] The passing of lithium containing solution to the second purification step produces a filtrate or permeate that is enriched in relative terms in lithium ions, providing the further purified lithium containing solution.

[0035] Preferably, the second purification step is conducted under pressure. The pressure may be 10 bar.

[0036] Preferably, the further purified lithium containing solution is suitable for use in the production of battery grade lithium chemicals.

[0037] In one form, the graphene is provided as a graphene oxide membrane formed in turn from graphite oxide powder. The graphene oxide membrane may preferably be supported on a first support that is in turn located in an aperture of a second support.

[0038] Preferably the first support is an anodic alumina disc. Still preferably, the second support is a copper plate.

[0039] In one form the graphene is provided as a reduced graphene oxide membrane. The graphene oxide membrane may preferably be reduced by way of exposure to ascorbic acid.

[0040] The area used for pressure filtration is preferably about 1 – 2 cm². Preferably, the membranes may be further supported by a porous substrate. In one form the porous substrate may be provided in the form of polyether sulfone (PES).

[0041] Preferably, an adhesive material is applied to the porous substrate to increase the bond between the substrate and the graphene material. Still preferably, the adhesive material is provided in the form of a polymer. Still further preferably, the polymer is a positively charged polymer.

[0042] In one form the positively charged polymer is polydiallyldimethylammonium chloride.

[0043] Preferably, the graphene membrane has a thickness of between 30 to 200 nm. Still preferably, the thickness of the graphene membrane is 150 to 200 nm.

[0044] Preferably, the salt rejection achieved by the second purification step is 20% or greater as measured by the conductivity of the permeate relative to that of the part-purified lithium containing solution.

[0045] Still preferably, lithium is the least rejected ion or salt of the second purification step.

[0046] In one form, the first and second purification steps may comprise one or more stages, passes or repeats of contact or exposure between the lithium containing solution passed to them and the adsorbent or filter medium, respectively.

[0047] Preferably, the lithium hydroxide product produced in the electrolysis step is passed to a crystallisation step in which lithium hydroxide monohydrate is crystallised.

[0048] The electrolysis step is preferably conducted by passing the substantially purified lithium solution to one or more electrolytic cells or electrolyzers to convert the lithium present to lithium hydroxide.

[0049] Preferably, substantially only lithium chloride and water are consumed in the electrolysis step, thereby producing substantially only lithium hydroxide, chlorine and hydrogen as products. Between 6 to 20 electrolyzers are preferably provided in the electrolysis step.

[0050] The chlorine and hydrogen produced in the electrolysis step are preferably combined to produce HCl acid.

[0051] In one form, the electrolysis step of the present invention is conducted using chlor-alkali technology at about or less than 50°C and a current efficiency of greater than about 70%.

[0052] In accordance with the present invention there is further provided a process for the synthesis of a titanate adsorbent.

[0053] Preferably, the titanate adsorbent is provided in the form of sodium titanate ($\text{Na}_2\text{Ti}_3\text{O}_7$) and hydrogen titanate (H_2TiO_3).

[0054] Still preferably, the titanate adsorbent formed in accordance with this process is suitable for the extraction of lithium from a lithium containing solution. The lithium containing solution may be a brine. The brine may contain impurities from the group of sodium, potassium, magnesium, calcium and borate.

Brief Description of the Drawings

[0055] The present invention will now be described, by way of example only, with reference to one embodiment thereof and the accompanying drawings, in which:-

Figure 1 is an XRD pattern of a pristine TiO_2 powder;

Figure 2 is a TEM image of pristine TiO_2 ;

Figure 3 is an XRD Pattern of a $\text{Na}_2\text{Ti}_3\text{O}_7$ prepared at 120°C ;

Figure 4 is an XRD Pattern of an $\text{Na}_2\text{Ti}_3\text{O}_7$ prepared at 150°C ;

Figure 5 is a an XRD Pattern of $\text{Na}_2\text{Ti}_3\text{O}_7$ prepared at 180°C ;

Figure 6 is a TEM image of $\text{Na}_2\text{Ti}_3\text{O}_7$ Prepared at 120°C ;

Figure 7 is a TEM image of $\text{Na}_2\text{Ti}_3\text{O}_7$ Prepared at 150°C ;

Figure 8 is a TEM image of $\text{Na}_2\text{Ti}_3\text{O}_7$ Prepared at 180°C ;

Figure 9 is the XRD patterns of Li_2TiO_3 and H_2TiO_3 as per Example 3;

Figure 10 is a TEM image of Li_2TiO_3 ;

Figure 11 is a TEM image of H_2TiO_3 ;

Figure 12 is an XRD pattern of $\text{Na}_2\text{Ti}_3\text{O}_7$ (Synthesised at 120°C) after Adsorption Test;

Figure 13 is an XRD pattern of $\text{Na}_2\text{Ti}_3\text{O}_7$ (Synthesised at 120°C) after Adsorption Test;

Figure 14 is a TEM image of $\text{Na}_2\text{Ti}_3\text{O}_7$ (Synthesised at 120°C) after Adsorption Test;

Figure 15 is an XRD pattern of $\text{Na}_2\text{Ti}_3\text{O}_7$ (Synthesised at 150°C) after Adsorption Test;

Figure 16 is an XRD pattern of $\text{Na}_2\text{Ti}_3\text{O}_7$ (Synthesised at 150°C) after Adsorption Test;

Figure 17 is TEM image of $\text{Na}_2\text{Ti}_3\text{O}_7$ (Synthesised at 150°C) after Adsorption Test;

Figure 18 is an XRD pattern of $\text{Na}_2\text{Ti}_3\text{O}_7$ (Synthesised at 180°C) after Adsorption Test;

Figure 19 is an XRD pattern of $\text{Na}_2\text{Ti}_3\text{O}_7$ (Synthesised at 180°C) after Adsorption Test;

Figure 20 is TEM image of $\text{Na}_2\text{Ti}_3\text{O}_7$ (Synthesised at 180°C) after Adsorption Test;

Figure 21 is a kinetic adsorption test of sodium titanate $\text{Na}_2\text{Ti}_3\text{O}_7$ sorbent synthesizes at 150°C in 100 ml brine solution (~ 300 ppm Li);

Figure 22 is a kinetic adsorption test of sodium titanate $\text{Na}_2\text{Ti}_3\text{O}_7$ sorbent synthesizes at 150°C in 100 ml brine solution (~ 300 ppm Li);

Figures 23(a) to 23(d) are the XRD characterisations for sodium titanate ($\text{Na}_2\text{Ti}_3\text{O}_7$) synthesised at 150°C sorbents, observed at 4 sampling times;

Figure 24 shows BET surface areas of sodium titanate synthesizes at 120°C , 150°C and 180°C observed before and after adsorption;

Figure 25 shows the kinetics of 3g sodium titanate sorbent prepared at 150°C ($\text{Na}_2\text{Ti}_3\text{O}_7$ 150) for 100 mL brine solution with different concentrations of Li^+ ions and at different times of adsorption;

Figure 26 shows the kinetics of 10g sodium titanate sorbent prepared at 150°C ($\text{Na}_2\text{Ti}_3\text{O}_7$ 150) for 100 mL brine solution with different concentrations of Li^+ ions and at different times of adsorption;

Figure 27 shows an increased in amount of sorbent to 100 g/100 mL of brine solution (sorbent prepared at 150°C - $\text{Na}_2\text{Ti}_3\text{O}_7$ 150) for different concentrations of Li^+ ions and at different times of adsorption;

Figure 28 shows the results of the kinetic adsorption tests of hydrogen titanate sorbent (H_2TiO_3) in sorbent to solution ratio: 3g - 100mL brine solution (~300 ppm Li);

Figure 29 shows the results of the kinetic adsorption tests of hydrogen titanate sorbent (H_2TiO_3) in sorbent to solution ratio: 10g – 100mL brine solution (~300 ppm Li);

Figure 30 shows the results of the kinetic adsorption tests of hydrogen titanate sorbent (H_2TiO_3) in sorbent to solution ratio: 100g – 1000mL brine solution (~300 ppm Li);

Figure 31 shows XRD data of the sorbent hydrogen titanate sorbent (H_2TiO_3) before and after adsorption at different times;

Figure 32 shows BET surface area data of the sorbent hydrogen titanate sorbent (H_2TiO_3) before and after adsorption;

Figure 33 shows the reaction kinetics of 3 g hydrogen titanate sorbent (H_2TiO_3), 100 mL brine solution with different concentrations of with different concentrations of Li^+ ions;

Figure 34 shows the reaction kinetics of 10 g hydrogen titanate sorbent (H_2TiO_3), 100 mL brine solution with different concentrations of with different concentrations of Li^+ ions;

Figure 35 shows the reaction kinetics of 100 g hydrogen titanate sorbent (H_2TiO_3), 1000 mL brine solution with different concentrations of with different concentrations of Li^+ ions;

Figure 36 shows the results of kinetic desorption testing for TNT-120;

Figure 37 shows the results of kinetic desorption testing for TNT-150;

Figure 38 shows the results of kinetic desorption testing for TNT-180;

Figure 39 shows the desorption data for hydrogen titanate sorbent (H_2TiO_3);

Figure 40 shows XRD patterns of TNT-120 sorbent after adsorption in 300 ppm Li^+ solution;

Figure 41 shows XRD patterns of TNT-150 sorbent after adsorption in 300 ppm Li^+ solution;

Figure 42 shows XRD patterns of TNT-180 sorbent after adsorption in 300 ppm Li^+ solution;

Figure 43 shows XRD patterns of H_2TiO_3 sorbent after adsorption in 300 ppm Li^+ solution;

Figure 44 shows TEM images of TNT-120 sorbents after desorption with 0.05M HCl at 25 °C;

Figure 45 shows TEM images of TNT-150 sorbents after desorption with 0.05M HCl at 25 °C;

Figure 46 shows TEM images of TNT-180 sorbents after desorption with 0.05M HCl at 25 °C;

Figure 47 shows TEM images of H_2TiO_3 sorbents after desorption with 0.05M HCl at 25 °C;

Figure 48 shows Na^+ and Cl^- ion permeation through a GO membrane;

Figure 49 shows the filtration performance of modified GO membranes with different thickness (Figure 49a) and different reduction time (Figure 49b);

Figure 50 shows the concentration of salts in a brine solution before and after filtration through a modified GO membrane, where the Y-axis – log scale and S1 and S2 represent data from two different membranes, the membrane used being 200 nm thick and 30 minute rGO;

Figure 51 shows the current efficiency data based on caustic collection and gas analysis for the electrolysis step;

Figure 52 shows the cell voltage results, and the LiOH concentration exiting the cell during each run, for the electrolysis step of Figure 51; and

Figure 53 shows the DC energy consumption data for the electrolysis step of Figure 51.

Best Mode(s) for Carrying Out the Invention

[0056] The present invention provides a combined processing method for the purification of lithium containing solutions, the method comprising the method steps of:

- a) passing a lithium containing solution to one or more purification steps to produce a substantially purified lithium chloride solution; and
- b) passing the substantially purified lithium chloride solution of step a) to an electrolysis step in which lithium hydroxide monohydrate is produced,

wherein the one or more purification steps comprises either or both of a first purification step in which the lithium containing solution is contacted with a titanate adsorbent whereby lithium ions are adsorbed thereon whilst rejecting substantially all other cations, the recovery of lithium from the adsorbent providing a part-purified lithium containing solution, and a second purification step in which a graphene based filter medium is utilised to provide a further purified lithium containing solution.

[0057] In one form of the present invention the part-purified lithium containing solution produced in the first purification step is passed in whole or part to the second purification step, such that the combined method comprises both purification steps.

[0058] In one form, the lithium containing solution is a lithium containing brine. The brine to be treated initially contains impurities from the group of sodium, potassium, magnesium, calcium and borate. In one form of the present invention the brine contains lithium in the range of about 500 to 1500 ppm, and impurities including magnesium in the range of about 0.15% to 0.30%, calcium in the range of about 0.05% to 0.1%, sodium in the range of about 8 to 10%, potassium in the range of about 0.7% to 1.0%, and borate in the range of about 0.15% to 0.20%. In a more preferred form of the present invention, the brine contains about 700 ppm lithium, about 0.19% magnesium,

about 0.09% calcium, about 8.8% sodium, about 0.8% potassium and about 0.18% borate.

[0059] The adsorbent is provided in the form of either a hydrated titanium dioxide or a sodium titanate. In one form of the present invention the hydrated titanium dioxide is produced from titanium dioxide.

[0060] The process in turn produces a substantially pure lithium chloride solution. The impurity concentration of the substantially pure lithium chloride solution does not exceed about 20 ppm.

[0061] The brine solution is preferably adjusted to a pH of 7 through the addition of a base. The base is preferably provided in the form of sodium hydroxide.

[0062] The contact between the brine solution and the adsorbent preferably takes place at or about room or ambient temperature. Room temperature is understood to be between about 20°C to 28°C.

[0063] In one form of the present invention the brine is collected into a vessel and cooled to room temperature prior to its exposure to the adsorbent. The contact or residence time between the brine solution and the adsorbent is between about 4 to 24 hours.

[0064] The contact or residence time between the brine solution and the adsorbent is:

- a) between about 8 to 24 hours;
- b) between about 20 to 24 hours; or
- c) between about 8 to 16 hours.

[0065] It is to be understood that the contact time is to some extent dependent upon additional variables including reactor size and shape.

[0066] The recovery of lithium from the adsorbent is achieved through the regeneration of the adsorbent by the addition of an acid solution and the adsorbed lithium is extracted

to provide the part purified lithium containing solution. The acid solution is a solution of hydrochloric acid.

[0067] The amount of lithium extracted from the adsorbent through exposure to the acid solution is greater than about 90%. For example, the amount of lithium extracted from the adsorbent through exposure to the acid solution is about 100% of the adsorbed lithium.

[0068] The graphene based filter medium of the second purification step comprises a graphene membrane formed of one or more graphene, graphene oxide and/or reduced graphene oxide and to which the part-purified lithium containing solution is presented.

[0069] The passing of the part purified lithium containing solution to the second purification step produces a filtrate or permeate that is enriched in relative terms in lithium ions, providing the further purified lithium containing solution.

[0070] The second purification step is conducted under pressure. The pressure may be at or about 10 bar.

[0071] The further purified lithium containing solution is suitable for use in the production of battery grade lithium chemicals.

[0072] In one form, the graphene is provided as a graphene oxide membrane formed in turn from graphite oxide powder. The graphene oxide membrane may be supported on a first support that is in turn located in an aperture of a second support. The first support is, for example, an anodic alumina disc. The second support is, for example, a copper plate.

[0073] In one form the graphene is provided as a reduced graphene oxide membrane. The graphene oxide membrane may be reduced by way of exposure to ascorbic acid.

[0074] The area used for pressure filtration is about 1 – 2 cm². The membranes may be further supported by a porous substrate. In one form the porous substrate may be provided in the form of polyether sulfone (PES).

[0075] An adhesive material may be applied to the porous substrate to increase the bond between the substrate and the graphene material. The adhesive material is, for example, provided in the form of a polymer. The polymer is, in one form, a positively charged polymer, for example polydiallyldimethylammonium chloride.

[0076] The graphene membrane may have a thickness of between 30 to 200 nm. For example, the thickness of the graphene membrane is 150 to 200 nm.

[0077] The level of salt rejection achieved by the second purification step is 20% or greater as measured by the conductivity of the permeate relative to that of the partially purified lithium containing solution. Lithium is the least rejected ion or salt of the second purification step.

[0078] In one form, the first and second purification steps may comprise one or more stages, passes or repeats of contact or exposure between the lithium containing solution passed to them and to the adsorbent or filter medium, respectively.

[0079] The electrolysis step is conducted by passing the substantially purified lithium solution, for example a lithium chloride solution, to one or more electrolytic cells or electrolyzers to convert the lithium present, for example present as lithium chloride, to lithium hydroxide. For example, 6 to 20 electrolyzers may be provided, in which substantially only lithium chloride and water are consumed, thereby producing substantially only lithium hydroxide, chlorine and hydrogen as products. The chlorine and hydrogen so produced may be combined to produce HCl acid for use elsewhere bringing potential efficiencies and potential cost savings.

[0080] In one embodiment the electrolysis step is conducted using chlor-alkali technology at about or less than 50°C. This has been found by the Applicants to provide a current efficiency of greater than about 70%, for example 75%. The relatively low temperature and high current efficiency is understood to be due to the quality or purity of the substantially purified lithium solution being fed to the electrolyzers of the electrolysis step. Both identified advantages bring beneficial cost implications. It is noted elsewhere that the purification steps of the present invention are capable of reduced impurity levels in lithium containing solutions to levels of less than 20 ppm.

[0081] The lithium hydroxide product produced in the electrolysis step is passed to a crystallisation step in which lithium hydroxide monohydrate is crystallised.

[0082] The present invention further provides a process for the synthesis of a titanate adsorbent. The titanate adsorbent is provided in the form of sodium titanate ($\text{Na}_2\text{Ti}_3\text{O}_7$) and hydrogen titanate (H_2TiO_3).

[0083] The titanate adsorbent formed in accordance with this process is suitable for the extraction of lithium from a lithium containing solution. The lithium containing solution may be a brine. The brine may contain impurities from the group of sodium, potassium, magnesium, calcium and borate.

[0084] The combined processing method for the purification of lithium containing solutions of the present invention may be further understood with reference to the following non-limiting examples, noting that either or both of the first and second purification steps are envisaged to be used in combination with the electrolysis step.

Example 1 – Synthesis of $\text{Na}_2\text{Ti}_3\text{O}_7$ nano-tubes/fibres

[0085] 150 g of TiO_2 (Anatase type) powder was mixed with 3L NaOH solution (10 mol/L), and kept stirring for 2 hours, then transferred to 5L autoclave and react at each of 120°C , 150°C , and 180°C for 48 h. Resulting $\text{Na}_2\text{Ti}_3\text{O}_7$ nano-tubes were washed using vacuum filtration until pH of filtrate was 7. The product weight after drying at 100°C was 175 g. This produced high purity $\text{Na}_2\text{Ti}_3\text{O}_7$ nanotubes (over 95% product are tubes); the nanotubes have the largest specific surface area of $232 \text{ m}^2/\text{g}$.

[0086] The sodium titanate was characterized by powder X-ray diffraction (XRD) and transmission electron microscopy (TEM) to confirm the morphological phase and structure.

[0087] In Figure 1 there is shown the XRD pattern of the pristine TiO_2 powder. This suggests that TiO_2 material contained mainly rutile (R) TiO_2 mixed with some anatase (A) phase.

[0088] In Figure 2 there is shown a TEM image of pristine TiO_2 is shown. It can be seen that the diameter of the TiO_2 particles is around 100~200 nm.

Synthesis and XRD – $\text{Na}_2\text{Ti}_3\text{O}_7$ (Sodium Titanate)

[0089] The XRD patterns of the Na-titanate exhibit apparent difference from the pristine TiO_2 powder. The XRD patterns of these samples are in good agreement with that of monoclinic $\text{Na}_2\text{Ti}_3\text{O}_7$ phase. The synthetic processes and XRD patterns of $\text{Na}_2\text{Ti}_3\text{O}_7$ samples prepared at different temperatures 120°C, 150°C and 180°C are provided below.

Synthesis of $\text{Na}_2\text{Ti}_3\text{O}_7$ at 120°C

[0090] 150 g TiO_2 powder was mixed with 3L NaOH solution (10 mol/L), and kept stirring for 2 h, then transferred to 5L autoclave and react at 120°C for 48 h. Resulting $\text{Na}_2\text{Ti}_3\text{O}_7$ nanotubes were washed with water using vacuum filtration until pH value of filtrate was 7. Product weight after drying at 100°C: 175 g.

[0091] The XRD Pattern of $\text{Na}_2\text{Ti}_3\text{O}_7$ Prepared at 120°C is shown in Figure 3.

Synthesis of $\text{Na}_2\text{Ti}_3\text{O}_7$ at 150°C

[0092] 150 g TiO_2 powder mixed with 3 L NaOH solution (10 mol/L), and kept stirring for 2 h, then transferred to 5 L autoclave and react at 150°C for 48 h. Resulting $\text{Na}_2\text{Ti}_3\text{O}_7$ nanotubes were washed with water using vacuum filtration until pH value of filtrate was 7. Product weight after drying: 171 g.

[0093] The XRD Pattern of $\text{Na}_2\text{Ti}_3\text{O}_7$ Prepared at 1500C is shown in Figure 4.

Synthesis of $\text{Na}_2\text{Ti}_3\text{O}_7$ at 180°C

[0094] 150 g TiO_2 powder mixed with 3 L NaOH solution (10 mol/L), and kept stirring for 2 h, then transferred to 5 L autoclave and react at 180°C for 48 h. Resulting $\text{Na}_2\text{Ti}_3\text{O}_7$ nanotubes were washed with water using vacuum filtration until pH value of filtrate was 7. Product weight after drying: 172 g.

[0095] The XRD Pattern of $\text{Na}_2\text{Ti}_3\text{O}_7$ Prepared at 1800C is shown in Figure 5.

TEM: $\text{Na}_2\text{Ti}_3\text{O}_7$

[0096] After the hydrothermal reaction, the TiO_2 particle morphology is changed. As can be seen clearly from the TEM images of the hydrothermal reaction products, the long tubes are well crystallized of layered Na-titanate according to the TEM images of the samples. A TEM image of $\text{Na}_2\text{Ti}_3\text{O}_7$ Prepared at 120⁰C is shown in Figure 6. A TEM image of $\text{Na}_2\text{Ti}_3\text{O}_7$ Prepared at 150⁰C is shown in Figure 7. A TEM image of $\text{Na}_2\text{Ti}_3\text{O}_7$ Prepared at 180⁰C is shown in Figure 8.

Synthesis of H_2TiO_3 nano-tubes/fibres

Example 2

[0097] 150 g of TiO_2 (Anatase type) and 13.9 g of Li_2CO_3 were mixed, ground and heated in an alumina crucible at a rate of ca 6⁰C/ min in air up to 700⁰C and maintained for the next 4 h. After cooling to room temperature, the solid powder (Li_2TiO_3) was treated with 0.2M HCl solution with occasional shaking for 24 h at room temperature (5 g solid in 1L HCl acid). The solid was separated by filtration, washed and deionized water until the filtrate was neutral, and allowed to dry at room temperature to obtain high purity H_2TiO_3 .

Example 3

[0098] Anatase type TiO_2 (15.0 g, Ti 0.187 mole) and Li_2CO_3 (13.9 g, Li 0.376 mole) were mixed, ground and heated in an alumina crucible at a rate of ca. 6⁰C/min in air up to 700⁰C and maintained for the next 4 h. After cooling to room temperature, the solid powder (Li_2TiO_3) was treated with 0.2 M HCl solution with occasional shaking for 24 h at room temperature (5 g of solid in 1L acid). The solid was separated by filtration, washed with deionized water until the filtrate was neutral and allowed to dry at room temperature to obtain the H_2TiO_3 .

[0099] The precursor (Li_2TiO_3) and (H_2TiO_3) sorbent was prepared through solid calcination method. XRD patterns of precursor and H_2TiO_3 sorbent matches the known literature.

[00100] TEM analysis indicates that H_2TiO_3 sorbent is mostly round shape nanoparticles and nano-rods with average size 200-400 nm. Li_2TiO_3 precursor exhibits similar structure as H_2TiO_3 sorbent suggesting that acid treatment has negligible impact on the morphology of the sorbent.

[00101] The surface area of synthesized H_2TiO_3 sorbent at $20.0 \text{ m}^2/\text{g}$ is far less than $\text{Na}_2\text{Ti}_3\text{O}_7$ nanotubes synthesized at 150°C ($232 \text{ m}^2/\text{g}$). The Brunauer-Emmett-Teller (BET) result is consistent with TEM analysis.

[00102] The XRD Patterns of Li_2TiO_3 and H_2TiO_3 are shown in Figure 9.

TEM: Li_2TiO_3

[00103] A TEM image of Li_2TiO_3 is shown at Figure 10.

TEM: H_2TiO_3

[00104] A TEM image of H_2TiO_3 is shown at Figure 11.

Example 4 - Sorbent Tests

[00105] A brine solution, the composition of which is described in the table below ($\sim 300 \text{ ppm Li}$), was chosen for the adsorption tests.

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Table 1 – Composition of brine/L:

Compound	Mass (g)
Na ₂ SO ₄	23.53
Na ₂ B ₄ O ₇ ·10H ₂ O	3.81
NaHCO ₃	0.32
NaCl	210.43
KCl	22.50
MgCl ₂ ·6H ₂ O	40.80
CaCl ₂	1.25
LiCl	1.92

Sodium Titanate (Na₂Ti₃O₇) Sorbent Behaviour

[00106] The kinetics of lithium adsorption by sodium titanate was determined by sampling the brine during adsorption at time intervals of 5min, 15min, 30min, 1hr, 2hr, 3hr, 4hr, 5hr, 6hr, 7hr, 8hr, 9hr, 10hr, 11hr, 12hr, 24hr (16 sampling times). The adsorption kinetics for all 9 sodium titanate sorbents was determined using brine solution of similar composition and no buffer. Analytical characterisation was done by ICP, XRD and BET methods on selected samples.

[00107] It was observed that the Li⁺ adsorption reached to its equilibrium in 5-15 minutes for most of the adsorption test.

[00108] XRD characterisation of the adsorbed sorbent confirmed that the structure remains unchanged, however weak characterization peaks of MgTiO_x (x=3 or 5) were observed because of heavy presence of Mg in the brine and affinity of sorbent towards Mg.

[00109] It was also observed that after Li⁺ uptake, the specific surface area of Na₂Ti₃O₇ decreases. Several observations and conclusions have also been made, including that Na₂Ti₃O₇ synthesized at 150°C shows the highest Li⁺ uptake (1.42 ± 0.1 mg/g) compared to the Na₂Ti₃O₇ synthesized at 120°C and 180°C, when a Brine solution of 300 ppm Li⁺ concentration is used. Further, after Li⁺ uptake, very small nanoparticles (2-3 nm) were found on the surface of sodium titanate sorbents as indicated in TEM images. The XRD analysis show that those nanoparticles are mostly

MgTiO_x (x=3 or 5), this is thought to be due to the high concentration of Mg²⁺ (about 5000 ppm) in the brine solution.

XRD Pattern of Na₂Ti₃O₇ (Synthesised at 120⁰C) after Adsorption Test

[00110] The Li brine (~300 ppm Li) 100 mL was adsorbed for 2 h in 3 g sorbent. The XRD pattern is shown in Figure 12.

[00111] The Li brine (~300 ppm Li) 100 mL was adsorbed for 2 h in 10 g sorbent also. The XRD pattern is shown in Figure 13.

[00112] The TEM images of Na₂Ti₃O₇ (synthesised at 120⁰C) collected after adsorption test in 100 mL of brine (~300 ppm Li) for 2 h in 3 g sorbent are shown in Figure 14.

XRD Pattern of Na₂Ti₃O₇ (Synthesised at 150⁰C) after Adsorption Test

[00113] The Li brine (~300 ppm Li) 100 mL was adsorbed for 2 h in 3 g sorbent. The XRD pattern is shown in Figure 15.

[00114] The Li brine (~300 ppm Li) 100 mL was adsorbed for 2 h in 10 g sorbent. The XRD pattern is shown in Figure 16.

[00115] The TEM images of Na₂Ti₃O₇ (synthesised at 150⁰C) collected after adsorption test in 100 mL of brine (~300 ppm Li) for 2 h in 3 g sorbent is provided in Figure 17.

XRD Pattern of Na₂Ti₃O₇ (Synthesised at 180⁰C) after Adsorption Test

[00116] The Li brine (~300 ppm Li) 100 mL was adsorbed for 2 h in 3 g sorbent. The XRD pattern is shown in Figure 18.

[00117] The Li brine (~300 ppm Li) 100 mL was adsorbed for 2 h in 10 g sorbent. The XRD pattern is shown in Figure 19.

[00118] The TEM images of $\text{Na}_2\text{Ti}_3\text{O}_7$ (synthesised at 180°C) collected after adsorption test in 100 mL of brine (~ 300 ppm Li) for 2 h in 3 g sorbent are shown in Figure 20.

[00119] ICP analysis results of sorption tests in for 3 g and 10 g sodium titanate sorbent in 100 ml brine solution (~ 300 ppm Li^+) after 2h are provided in the below table.

Table 2

Brine (~ 300 ppm Li)		Uptake (mg/g)	
<i>Adsorbent</i>	<i>Sorbent (g)-Solution (ml)</i>	<i>Li</i>	<i>Mg</i>
$\text{Na}_2\text{Ti}_3\text{O}_7$ (120°C)	3 g – 100 ml	0.68	4.43
	10 g – 100 ml	0.73	7.52
$\text{Na}_2\text{Ti}_3\text{O}_7$ (150°C)	3 g – 100 ml	1.42 ± 0.1	5.61
	10 g – 100 ml	1.30 ± 0.1	6.27
$\text{Na}_2\text{Ti}_3\text{O}_7$ (180°C)	3 g – 100 ml	0.41	1.2
	10 g – 100 ml	0.51	4.61

[00120] $\text{Na}_2\text{Ti}_3\text{O}_7$ (150°C) shows the best results on Li uptake at 1.42mg/ g of sorbent in 100 mL brine solution adsorbed for 2 hours.

[00121] The Kinetic adsorption tests of sodium titanate $\text{Na}_2\text{Ti}_3\text{O}_7$ sorbent synthesizes at 150°C in 100 ml brine solution (~ 300 ppm Li) are shown in Figures 21 and 22 confirming that the Li^+ adsorption reaches to its equilibrium in 5-15 minutes for most of the adsorption tests.

[00122] The XRD characterisation for sodium titanate ($\text{Na}_2\text{Ti}_3\text{O}_7$) synthesised at 150°C sorbents was observed at 4 of the sampling times, and shown in Figures 23 (a) to (d). It was observed that the structure of sorbent remains unchanged.

[00123] BET surface areas of sodium titanate synthesizes at 120°C , 150°C and 180°C were observed before and after adsorption and are shown in Figure 24.

[00124] With the exception of sodium titanate synthesised at 120°C which nearly remains unchanged within the experimental error variation, all other sodium titanate samples showed decrease in BET surface area after adsorption.

[00125] Li equilibrium adsorption for sodium titanate sorbents for different concentration of Li in brine was also studied. It was found that $\text{Na}_2\text{Ti}_3\text{O}_7$ sorbent synthesized at 150°C reaches the Li^+ uptake equilibrium of 4.65 mg/g at Li^+ concentration above 1,300 ppm when dispersed 3 g sorbent into 100 ml brine solution. An increase in the sorbent amount to 10 g, the uptake equilibrium was found to decrease to 2.5 mg/g.

[00126] $\text{Na}_2\text{Ti}_3\text{O}_7$ 120 and $\text{Na}_2\text{Ti}_3\text{O}_7$ 180 show much lower Li^+ uptake equilibrium below 1.5 mg/g at those concentrations of Li in brine.

[00127] The kinetics of 3g sodium titanate sorbent prepared at 150°C ($\text{Na}_2\text{Ti}_3\text{O}_7$ 150) for 100 mL brine solution with different concentrations of Li^+ ions and at different times of adsorption is shown in Figure 25. The maximum adsorption at 4.65 mg/g of sorbent may be achieved in 2 hours at 1,300 ppm Li concentration in brine.

[00128] The kinetics of 10g sodium titanate sorbent prepared at 150°C ($\text{Na}_2\text{Ti}_3\text{O}_7$ 150) for 100 mL brine solution with different concentrations of Li^+ ions and at different times of adsorption is shown in Figure 26. The adsorption of Li at ~4 mg/g of sorbent is lower than using 3 g of sorbent/ 100 mL of brine solution.

[00129] An increased in amount of sorbent to 100 g/100 mL of brine solution (sorbent prepared at 150°C - $\text{Na}_2\text{Ti}_3\text{O}_7$ 150) for different concentrations of Li^+ ions and at different times of adsorption is shown in Figure 27. The adsorption of Li decreases significantly.

Sorbent Behaviour of Hydrogen Titanate (H_2TiO_3)

[00130] Li adsorption kinetics for H_2TiO_3 sorbents was determined by sampling the brine during adsorption at time intervals of 5min, 15min, 30min, 1hr, 2hr, 3hr, 4hr, 5hr, 6hr, 7hr, 8hr, 9hr, 10hr, 11hr, 12hr, 24hr (16 sampling times). The adsorption kinetics for H_2TiO_3 sorbents was determined using just 300 ppm Li brine solution.

[00131] For analytical characterisation, ICP was performed for all samples. XRD characterisation was performed for half of the H_2TiO_3 sorbent at 4 of the sampling times.

BET characterisation was performed for the H_2TiO_3 sorbent synthesised before and after Li^+ adsorption.

[00132] It was observed that the Li^+ adsorption reached to its equilibrium after 30 minutes for H_2TiO_3 sorbent, which was found to be slower than $\text{Na}_2\text{Ti}_3\text{O}_7$ nanotubes synthesized at 150°C .

[00133] XRD patterns of H_2TiO_3 after Li^+ adsorption suggests that the impact of adsorption process on H_2TiO_3 sorbent is negligible.

[00134] After Li^+ uptake, the specific surface area of H_2TiO_3 sorbent was found to be decreased from $20 \text{ m}^2/\text{g}$ to $18.1 \text{ m}^2/\text{g}$.

[00135] The Figures 28 to 30 show the results of the kinetic adsorption tests of hydrogen titanate sorbent (H_2TiO_3) in different sorbent to solution ratio: 3g - 100mL, 10g – 100mL, and 100g – 1000mL brine solution ($\sim 300 \text{ ppm Li}$), respectively.

[00136] Figure 31 shows XRD data of the sorbent hydrogen titanate sorbent (H_2TiO_3) before and after adsorption at different times.

[00137] Figure 32 shows BET surface area data of the sorbent hydrogen titanate sorbent (H_2TiO_3) before and after adsorption.

[00138] The Li equilibrium adsorption for a hydrogen titanate sorbent was observed for different brine concentrations. ICP characterisation was performed for all the samples.

[00139] It was observed that H_2TiO_3 sorbent reaches the Li^+ uptake equilibrium of 4.4 mg/g at Li^+ concentration of 500 ppm when dispersed 3 g sorbent into 100 ml brine solution. Neither increasing nor decreasing Li^+ concentration leads to reduced Li^+ uptake capacity. Increase the sorbent amount to 10 g , the uptake equilibrium is decreased to 2.8 mg/g . The results suggest H_2TiO_3 sorbent exhibits better Li^+ uptake at relatively low Li^+ concentration ($300\text{--}700 \text{ ppm}$) while $\text{Na}_2\text{Ti}_3\text{O}_7\text{-150}$ sorbent exhibits better performance at high Li^+ concentration ($900\text{--}1500 \text{ pm}$). When using large scale of

sorbent 100 g H_2TiO_3 to large scale of brine solution (1000 ml), the sorption capacity is rather low up to 1.3 mg/g only.

[00140] Figure 33 shows the reaction kinetics of 3 g hydrogen titanate sorbent (H_2TiO_3), 100 mL brine solution with different concentrations of with different concentrations of Li^+ ions.

[00141] Figure 34 shows the reaction kinetics of 10 g hydrogen titanate sorbent (H_2TiO_3), 100 mL brine solution with different concentrations of with different concentrations of Li^+ ions.

[00142] Figure 35 shows the reaction kinetics of 100 g hydrogen titanate sorbent (H_2TiO_3), 1000 mL brine solution with different concentrations of with different concentrations of Li^+ ions.

Example 5 - Recovery of Li/Regeneration of Sorbents

[00143] Recovery of Li/ Regeneration of sorbents for different regeneration conditions (limited sorbent/brine combinations) was studied. The combination of the 4 titanate sorbents and 3 brine solutions were selected for assessment of Li recovery and sorbent regeneration. The hydrogen titanate sorbent with the same 2 brine solutions was also tested. All samples were tested under 0.05 M and 0.1 M HCl solution at 25°C and 60°C respectively. Regeneration kinetics were determined by sampling the solution at time intervals of 5 min, 15 min, 30 min, 1 h, 2h, 3 h, 4 h, 5 h, 6 h, 7h, 8h, 9 h, 10 h, 11 h, 12 h, and 24 h.

[00144] Analytical characterisation was performed using ICP (inductively coupled plasma atomic emission spectroscopy), XRD (x-ray diffraction) and TEM (transmission electron microscopy).

[00145] The observations were that the Li^+ recovery amount from sodium titanate synthesized at 150°C sorbent was the highest at 1.4 mg/g during all samples used for this recovery test, which are below 1.0 mg/g. ICP data of Li^+ recovery kinetic data indicates that, when using brine solution with the composition as above, the Li^+ desorption reached equilibration at 5 mins for sodium titanate synthesized at 150°C and

30 mins for H_2TiO_3 sorbent ,respectively. The 0.1 M HCl solution exhibited superior desorption property compared with the diluted HCl solution (0.05 M) only except with H_2TiO_3 sorbent. The high desorption temperature (60°C) can increase the Li^+ desorption equilibration compared with that of room temperature.

[00146] According to the XRD characterization, 0.05 M HCl has negligible impact on the crystal structure of titanate nanotube sorbents. However, the XRD patterns suggests that concentrated HCl solution (0.1 M) can convert the sodium titanate to hydrogen titanate and anatase TiO_2 phase. TEM images of 4 sorbents after desorption at 25°C using 0.05 M HCl suggested the unchanged morphology of 4 sorbents.

Example 6 - Kinetic desorption tests

Sodium Titanate Synthesized at 120°C (TNT 120)

[00147] 10 g of the adsorbed sorbent was dispersed in 100 ml recovery solutions of 0.05M HCl and 0.1M HCl, respectively. Two different desorption temperatures were applied to find the influence of temperature. The four groups of desorption data are plotted together for a clear comparison.

[00148] As shown iin Figure 36, the higher concentration of HCl recovery solution exhibited the higher recovery amount of Li^+ from the used sodium titanate synthesized at 120°C (TNT 120). The elevated desorption temperature (60°C) is able to increase the Li^+ recovery, but not significantly. The triangles are desorption data over time using 0.05 M HCl solution at 25°C . The squares are desorption data over time using 0.05 M HCl solution at 60°C . The diamonds are desorption data over time using 0.1 M HCl solution at 25°C . The inverted triangles are desorption data over time using 0.1 M HCl solution at 60°C .

[00149] Element desorption from TNT-120 sorbent after adsorption with 10 g sorbent after 24 h is provided in the table below.

Table 3

Adsorbent	Desorption agent	Desorption temperature	Element release (mg/L)					
			Li	B	Ca	K	Mg	Na
TNT-120	0.05 M HCl	25°C	0.25	0.14	0.03	0.56	0.02	11.7
TNT-120	0.1 M HCl	25°C	0.88	0.17	5.49	5.73	2.43	39.7
TNT-120	0.05 M HCl	60°C	0.56	0.42	0.03	2.81	0.30	54.91
TNT-120	0.1 M HCl	60°C	0.95	0.18	5.8	5.67	1.9	41.5

Sodium Titanate Synthesized at 150°C (TNT 150)

[00150] 10 g of the sorbent TNT 150 was dispersed in 100 ml recovery solutions of 0.05M HCl and 0.1M HCl respectively. Two different desorption temperatures were applied. The four groups of desorption data are plotted together for a clear comparison.

[00151] The Li⁺ recovery amount from TNT-150 sorbent is the highest (1.4 mg/g) during all samples used for this recovery test.

[00152] At a same temperature, the higher concentration of HCl recovery solution exhibited the higher recovery amount of Li⁺ from the used TNT-150 sorbents, as shown in Figure 37. The elevated desorption temperature (60°C) is able to increase the Li⁺ recovery significantly, this is quite different from the other recovered samples. The triangles are desorption data over time using 0.05 M HCl solution at 25°C. The squares are desorption data over time using 0.05 M HCl solution at 60°C. The diamonds are desorption data over time using 0.1 M HCl solution at 25°C. The inverted triangles are desorption data over time using 0.1 M HCl solution at 60°C.

[00153] The following table depicts the element desorption from TNT-150 sorbent after adsorption brine solution with 10 g sorbent after 24 h.

Table 4

Adsorbent	Desorption agent	Desorption temperature	Element release (mg/L)					
			Li	B	Ca	K	Mg	Na
TNT-150	0.05 M HCl	25°C	0.488	0.37	0.03	2.6	0.22	48.59
TNT-150	0.1 M HCl	25°C	0.7035	0.39	6.07	6.38	1.09	71.96
TNT-150	0.05 M HCl	60°C	0.81	0.38	0.26	7.04	0.86	75.87
TNT-150	0.1 M HCl	60°C	1.29	0.38	0.27	3.01	1.01	75.76

Sodium Titanate Synthesized at 180°C (TNT 180)

[00154] The collected sodium titanate sorbent TNT-180 after adsorption in brine solution, 10g dispersed in 100 ml recovery solutions of 0.05M HCl and 0.1M HCl, respectively. Two different desorption temperatures were applied. The four groups of desorption data are plotted together for a clear comparison and shown in Figure 38.

[00155] The higher concentration of HCl recovery solution exhibited the higher recovery amount of Li⁺ from the used TNT-180 sorbents.

[00156] The elevated desorption temperature (60°C) did not show a clear increase of Li⁺ recovery. The triangles are desorption data over time using 0.05 M HCl solution at 25°C. The squares are desorption data over time using 0.05 M HCl solution at 60°C. The diamonds are desorption data over time using 0.1 M HCl solution at 25°C. The inverted triangles are desorption data over time using 0.1 M HCl solution at 60°C.

[00157] The following table depicts the element desorption from TNT-180 sorbent after adsorption in brine solution with 10 g sorbent after 24 h.

Table 5

Adsorbent	Desorption agent	Desorption temperature	Element release (mg/L)					
			Li	B	Ca	K	Mg	Na
TNT-180	0.05 M HCl	25°C	0.3347	0.11	0.01	1.05	0.03	29.60
TNT-180	0.1 M HCl	25°C	0.832	0.11	1.70	2.60	0.44	80.06
TNT-180	0.05 M HCl	60°C	0.4916	0.13	0.02	1.08	0.09	37.72
TNT-180	0.1 M HCl	60°C	1.041	0.15	1.66	3.03	0.38	94.96

Hydrogen Titanate

[00158] The collected hydrogen titanate sorbent (H_2TiO_3) after adsorption in brine solution, 10g sorbent was dispersed in 100 ml recovery solutions of 0.05M HCl and 0.1M HCl, respectively. Two different desorption temperatures were applied. The four groups of desorption data are plotted together for a clear comparison, as shown in Figure 39.

[00159] The different concentration of recovery solution or different recovery temperatures do not show a significant impact on the Li^+ recovery as it shown to other sodium titanate samples. Figure 39 shows kinetic desorption test of H_2TiO_4 sorbent after adsorption in brine solution. The triangles are desorption data over time using 0.05 M HCl solution at 25°C; the squares are desorption data over time using 0.05 M HCl solution at 60°C; the diamonds are desorption data over time using 0.1 M HCl solution at 25°C; the inverted triangles are desorption data over time using 0.1 M HCl solution at 60°C.

[00160] The following table shows element desorption from H_2TiO_4 sorbent after adsorption in brine solution with 10 g sorbent after 24 h.

Table 6

Adsorbent	Desorption agent	Desorption temperature	Element release (mg/L)					
			Li	B	Ca	K	Mg	Na
H ₂ TiO ₃	0.05 M HCl	25°C	0.731	0.004	0.05	0.10	0.016	1.90
H ₂ TiO ₃	0.1 M HCl	25°C	0.795	0.01	0.08	0.14	0.03	2.50
H ₂ TiO ₃	0.05 M HCl	60°C	0.8085	0.006	0.07	0.20	0.03	2.28
H ₂ TiO ₃	0.1 M HCl	60°C	0.7554	0.02	0.10	0.23	0.10	2.03

XRD Analysis

[00161] The XRD patterns suggested that concentrated HCl solution (0.1 M) can convert the sodium titanate TNT-120 and TNT-150 to hydrogen titanate and anatase TiO₂ phase slightly. TNT-180 has a more significant phase transformation, probably not feasible for repeated use. The possible impact of this slight phase change of sorbent in HCl solution to the next cycle Li⁺ uptake and recovery may explored in the future study.

XRD of TNT-120 after Li recovery

[00162] Figure 40 shows XRD patterns of TNT-120 sorbent after adsorption in 300 ppm Li⁺ solution. From the bottom, the first line is original TNT-120. The second line is TNT-120 after desorption using 0.05 M HCl solution at 25°C. The third line is TNT-120 after desorption using 0.1 M HCl solution at 25°C. The fourth line is TNT-120 after desorption using 0.05 M HCl solution at 60°C. The top line TNT-120 after desorption using 0.1 M HCl solution at 60°C.

XRD of TNT-150 after Li recovery

[00163] Figure 41 shows the XRD patterns of TNT-150 sorbent after adsorption in 300 ppm Li⁺ solution. Reading from the bottom, the first line is original TNT-150. The second line is TNT-150 after desorption using 0.05 M HCl solution at 25°C. The third line is TNT-150 after desorption using 0.1 M HCl solution at 25°C. The fourth line is

TNT-150 after desorption using 0.05 M HCl solution at 60°C. The top line TNT-150 after desorption using 0.1 M HCl solution at 60°C.

XRD of TNT-180 after Li recovery

[00164] Figure 42 shows the XRD patterns of TNT-180 sorbent after adsorption in 300 ppm Li⁺ solution. Reading from the bottom, the first line is the original TNT-180. The second line is TNT-180 after desorption using 0.05 M HCl solution at 25°C. The third line is TNT-180 after desorption using 0.1 M HCl solution at 25°C. The fourth line is TNT-180 after desorption using 0.05 M HCl solution at 60°C. The top line is TNT-180 after desorption using 0.1 M HCl solution at 60°C.

XRD of H₂TiO₃ after Li recovery

[00165] Figure 43 shows the XRD patterns of H₂TiO₃ sorbent after adsorption in 300 ppm Li⁺ solution. Reading from the bottom up, the first line is the original H₂TiO₃. The second line is H₂TiO₃ after desorption using 0.05 M HCl solution at 25°C. The third line is H₂TiO₃ after desorption using 0.1 M HCl solution at 25°C. The fourth line is H₂TiO₃ after desorption using 0.05 M HCl solution at 60°C. The fifth line is H₂TiO₃ after desorption using 0.1 M HCl solution at 60°C.

Example 7 - TEM Analysis

TEM images of Desorbed TNT-120

[00166] TEM images of TNT-120 sorbents after desorption with 0.05M HCl at 25 °C are shown in Figure 44. The comparison of sorbent morphology before and after desorption indicates that the Li⁺ recovery process does not show significant impact on the nanofiber. TEM images of TNT-120 sorbent after desorption with 0.05M HCl at 25 °C under different resolution (a) 50 nm, (b) 100 nm, (c) 200 nm, (d) 500 nm are shown.

TEM images of Desorbed TNT-150

[00167] EM images of TNT-150 sorbents after desorption with 0.05M HCl at 25 °C are shown in Figure 45. The comparison of sorbent morphology before and after desorption indicates that the Li⁺ recovery process does not show significant impact on

the nanofiber. TEM images of TNT-150 sorbent after desorption with 0.05M HCl at 25 °C under different resolution (a) 50 nm, (b) 100 nm, (c) 200 nm, (d) 500 nm are shown.

TEM images of Desorbed TNT-180

[00168] The TEM images of TNT-180 sorbents after desorption with 0.05M HCl at 25 °C are shown in Figure 46. The TNT-180 nanotubes are relatively large than TNT-120 and TNT-150, therefore low resolution. The comparison of sorbent morphology before and after desorption indicates that the Li⁺ recovery process does not show significant impact on the nanofiber. TEM images of TNT-180 sorbent after desorption with 0.05M HCl at 25 °C under different resolution (a) 50 nm, (b) 500 nm, (c) 1000 nm, (d) 2000 nm are shown.

TEM images of H₂TiO₃

[00169] The TEM images of H₂TiO₃ sorbents after desorption with 0.05M HCl at 25 °C are shown in Figure 47. The H₂TiO₃ sorbents are still particle aggregations over 100 nm, therefore. TEM images above 200 nm are collected as shown in the following figure. The comparison of sorbent morphology before and after desorption indicates that the Li⁺ recovery process removed the hand-shape particles from original sorbent. It is inferred that the hand-shape particles are Li₂CO₃ that dissolved by HCl solution, the amorphous particles aggregations, on the other hand, are H₂TiO₃ nanoparticles and their morphology is not influenced by desorption processes. TEM images of TNT-180 sorbent after desorption with 0.05M HCl at 25 °C under different resolution (a) and (b) 200 nm, (c) 500 nm, (d) 1000 nm is shown.

Example 8 – Brine Treatment with Adsorbents

[00170] Both sodium titanate (Na₂Ti₃O₇) and hydrogen titanate (H₂TiO₃) are, as noted above, preferred forms of the adsorbents used in the process of the present invention. Suitable sodium titanate (Na₂Ti₃O₇) and/or hydrogen titanate (H₂TiO₃) were synthesised as per methods described above. The function of the adsorbent material in the process of the present invention, without being limited by theory, is to absorb lithium ions from the LiCl brine and thereby rejecting the impurities, including competing cations.

[00171] The adsorbent ($\text{Na}_2\text{Ti}_3\text{O}_7$ and/or H_2TiO_3) used in this embodiment of the present invention may advantageously be placed in a series of column. Further, the adsorbent may be placed in a series of columns and the brine solution may be directed through this series of columns. In other preferred embodiments the adsorbent columns may be placed before the brine solution.

[00172] The lithium containing brine with the composition stated above was placed in a beaker. The adsorbent ($\text{Na}_2\text{Ti}_3\text{O}_7$ or H_2TiO_3) was packed in a series of vertical columns. The amount of adsorbent top pack in the series of columns to treat a particular brine was selected to adsorb maximum Li from the brine in provided series of columns as per data obtained from our R&D and stated above.

[00173] The brine was passed through the series of vertical columns and retained for 5 minutes to several hours for complete adsorption of lithium in the adsorbent packed columns. After this, the lithium adsorbed in the adsorbent was stripped from the adsorbent using a dilute HCl acid the optimum strength as discussed and provided above. The stripped solution was analysed for the concentration of Li and all other impurities such as B, Na, K, Ca and Mg. The lithium was found to be extracted at >90% from the brine.

[00174] The following table shows the comparative analyses of the original brine solution before feeding to the adsorbents and after desorbed from the adsorbents.

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Table 7

Elements	Original Brine ppm	Desorbed Brine ppm $\text{Na}_2\text{Ti}_3\text{O}_7$ (TNT 150)	Desorbed Brine ppm H_2TiO_3
Li	316	294	290
B	432	87	2.3
Ca	410	62	26
K	12,000	686	72
Mg	5,000	230	2
Na	100,000	17,266	820

[00175] An appropriate apparatus to be used in carrying out the first purification step of the present invention may be any manifold system whereby a lithium containing brine can be delivered to a series of columns containing an adsorbent and then ultimately collected in a receiving vessel. The apparatus may also have a means for drawing aliquots of LiCl for analysis. Such means may be a sample port comprising a resilient septum affixed in line to the apparatus. The apparatus may be composed of several vessels such as glass flasks, ceramic containers, metal containers or other typical non-reactive chemical reaction vessels. The vessels may be connected using non-reactive polymeric tubing, metal pipe or tube, or glass pipe or tube. The apparatus may be sectioned off using any type of valve stopcock or clamp depending on the composition of the tubing or piping.

[00176] The combined processing method for the purification of lithium containing solutions of the present invention further provides a method for the purification of semi-pure or part-purified LiCl solution obtained as may be produced as described above from a brine by using an adsorbent. The combined processing method further comprises passing the semi-pure LiCl solution obtained after desorption of adsorbent to

a graphene based filter medium, for example a graphene based membrane. The graphene based membrane is, in one form, prepared from graphene oxide (GO) or reduced graphene oxide (rGO), which allows appropriate permeation through the membrane.

Example 9 – Graphene Filter Medium Preparation – GO membrane

[00177] Graphene oxide dispersion is prepared by the ultra-sonication of graphite oxide powder in water and subsequent centrifugation. The vacuum filtration of the as-prepared solution on a first support, for example an anodic alumina disc, provides with subsequent drying a free-standing graphene oxide (GO) membrane. The GO membrane is then glued onto a second support, for example a copper plate having a 2 cm aperture provided in the centre thereof, for the conduct of permeation experiments.

Example 10 – Permeation Experiments

[00178] The permeation experiment was carried out such that the GO membranes, supported by the copper plate, were clamped between two O-rings and then fixed between feed and permeate compartments to provide a leak tight environment. The part-purified LiCl solution obtained after desorption from the adsorbent was used as feed and deionized water in the permeate side. As a result of the concentration gradient across the membrane, ions tend to diffuse through the membrane and reach the permeate side. Permeate solution is collected after 24 h and chemical analysis is conducted to quantify the ions in the permeate side.

[00179] The percentage of rejection for Mg^{2+} ion is 94 % whereas 45 % for Li^+ , Na^+ and K^+ ions. In Figure 48, it can be seen that Na^+ and Cl^- ion permeation through GO is faster than other ions. The Applicants understand this demonstrates the potential of GO membranes for the selective removal of salt from the concentrated brine solution.

[00180] The results are shown in the following table and in Figure 48.

Table 8

	Na (mg/L)	K (mg/L)	Mg (mg/L)	Li (mg/L)	Cl (mg/L)	SO4 (mg/L)
Feed	111,000	9,420	3,360	302	180,000	14,000
Feed (ICP data)	47630	5495	2614	224	102,870	9,778
Permeate (ICP data)	25,205	3,203	155	120	62,237	768
Ratio (feed:Permeate)	1.89	1.71	16.86	1.87	1.65	12.73

Pressure Filtration Using GO Membrane

[00181] To investigate the feasibility of using GO membrane in separating aqueous LiCl species from control aqueous brine or selective removal certain ions in the brine pressure filtration experiments were performed using a Sterlitech HP4750™ stirred cell. For pressure filtration, porous Poly ether sulfone (PES) was used as a substrate to increase the mechanical integrity of the membrane. To obtaining a reasonable flux we optimised the GO membrane thickness to 200-500 nm. The typical area used for pressure filtration was 1-2 cm². GO membrane on PES was then fixed inside the stirred cell using a rubber O-ring to avoid any possible leakage in the experiment. Brine solution was used as a feed solution and collected the water on filtrate side by applying a pressure of 10 bar using a compressed nitrogen gas cylinder.

[00182] Salt concentration on the filtrate side was analysed by checking the conductivity of the water solution and found that total salt rejection is 20%.

Preparation of rGO Membranes

[00183] GO membranes on PES substrates were found to be disintegrating after long time exposure to brine solution at high pressure and to resolve this issue we have partially reduced GO membrane with ascorbic acid. Partial reduction of GO decreased the amount of functional groups present in the membrane and subsequently reduced the hydrophilicity and wettability of the membrane. The ascorbic acid reduced graphene oxide (rGO) is found to be more stable in brine solution after long exposure.

Permeation through rGO membrane

[00184] As per the GO membranes referred to above, rGO membranes deposited on PES substrate (~5 cm dia membrane) were evaluated with pressure filtration. Even though the membrane is more stable after partial reduction, under high pressure, rGO layer from the PES got peeled off and damaged during the filtration. This suggests that reduced functional groups on rGO may have decreased the adhesion between the rGO layer and PES substrate. It is understood that increasing the adhesion of the rGO layer to PES will be possible by surface modification of PES with a polyelectrolyte.

Example 10 – Graphene Filter Medium Preparation – rGO membrane

[00185] An aqueous suspension of graphene oxide was prepared by dispersing millimeter-sized graphite oxide flakes (purchased from BGT Materials Limited) in distilled water using bath sonication for 15 hours. The resulting dispersion was centrifuged 6 times at 8000 rpm to remove the multilayer GO flakes. The concentration of as prepared GO solution was 0.1mg/ml. To improve the stability of GO membrane in brine solution we have partially reduced the GO with ascorbic acid. 1 ml of 0.17 mg/ml vitamin C was mixed with 1 ml GO solution and then the whole mixture was diluted to a volume of 20 ml. The pH of the mixed solution was adjusted to about 9-10 with 25% ammonia solution to promote the colloidal stability of the GO nanosheets. The solution was then heated at 90 degrees for 30 minutes in water bath to finish the reduction process.

[00186] Modified GO membranes were then prepared from the partially reduced GO (rGO) solution via vacuum filtration through a PES membrane with 0.22 um pore

size. In order to increase the adhesion between partially reduced GO membrane and PES substrate, we coated a very thin polymer film on the surface of the PES substrate. The polymer used was Poly(diallyldimethylammonium chloride), which is a positively charged polymer. The positively charged Poly(diallyldimethylammonium chloride) tightly bonded the GO membrane and PES substrate via the electrostatic forces. After coating, the coated PES membrane was stored in the vacuum oven for two hours at 50 °C before depositing the partially reduced GO via vacuum filtration.

[00187] Modified graphene-based membranes with improved adhesion and stability were prepared and tested for the membrane performance. Modified membranes were found stable in the brine solution and survived up to 20 Bar pressure. Membranes with different thickness, ranging from 30 nm to 200 nm, and different partial reduction conditions (reduction time) were prepared and their filtration properties via pressure filtration. Membranes having 150-200 nm thickness with 30 minute GO reduction time provided the best filtration performance. Typical water flow rate observed for 150-200 nm thickness were ~ 0.5 L/h/M2/Bar. All the filtration experiments were performed with 10 times diluted brine solution, because, due to the high osmotic pressure of the pure brine solution, no detectable water flux was observed. Figure 49 shows the filtration performance of modified GO membranes with different thickness (Figure 49a) and different reduction time (Figure 49b).

[00188] Figure 50 shows the concentration of salts in brine solution before and after filtration through the modified GO membrane. Y-axis – log scale. S1 and S2 represent data from two different membranes. Membrane used is 200 nm thick and 30 minute reduced GO.

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Table 9 – Salt content after and before filtration (membrane used – 200 nm, 30 minute reduced GO)

Sample	Ca (PPM)	K (PPM)	Li (PPM)	Mg (PPM)	Na (PPM)	B (PPM)
10 times diluted brine (feed)	60.48	850.37	73.54	125.07	11738.98	44.06
% content	0.46	6.5	0.57	0.97	91.0	0.34
After filtration	3.3	87	18.1	24.5	837.7	3.5
% content after filtration	0.33	8.9	1.9	2.5	85.9	0.35
Salt Rejection	94%	89%	75%	80%	92%	92%

[00189] The above experiments clearly show that all the salts in the brine solutions are rejected by the membrane with different rejection rate. Li salts gave least rejection (75%) with respect to other salts. The difference in rejection between Na and Li is ~ 20.

[00190] It is understood that the nano-channels and/or interlayer galleries formed between the nano-sheets of, for example, GO or rGO, act as ion-sieves.

Example 11 - Electrolysis

[00191] The present invention further provides an electrolysis step conducted on part-purified lithium chloride solution that is the product of either or both of the first and second purification steps as described hereinabove.

[00192] The combination of either or both of the first and second purification steps as described hereinabove and an electrolysis step allows the production of high purity lithium hydroxide.

[00193] The electrolysis is carried out at a current density of 5kA/m² at ~50°C. The electrolysis utilises N982™ ion exchange membranes from DuPont and is conducted in the range of 3.9-4.0V.

[00194] The feed lithium containing solution is obtained as a lithium chloride solution from either of the first or second purification steps described hereinabove, or potentially as the result of both the first and second purification steps if conducted in series. Whichever is the case, the solution is diluted to 300 g/L. The anolyte flow rate is adjusted to about 35 mL/min to achieve a depleted brine concentration of 200 g/L.

[00195] The electrolysis step is performed using the ion exchange membrane N982™ at a current density of 5kA/m² and at ~50°C. The current efficiency data based on caustic collection and gas analysis are presented in Figure 51, the cell voltage results are shown in Figure 52, and the DC energy consumption data shown in Figure 53. The LiOH concentration exiting the cell during each run is noted in Figure 52 also. The average cell voltage was in the range of 3.9-4.0V. The chlorated hypo-brine is treated with peroxide to destroy chlorate levels and the brine reused for electrolysis.

[00196] Membrane cell electrolysis showed an energy consumption of 3,500 kWh/ton of LiOH.H₂O, the cell voltage being in the range 3.9 to 4 V at 5kA/m², and the caustic current efficiency being ~75% with N982™ membranes.

[00197] The chloride concentration in the catholyte product LiOH was ~ 360 ppm. These chloride levels were removed during crystallization of LiOH catholyte using double crystallization process as described below.

[00198] The crystallization of LiOH.H₂O using LiOH catholyte produced by electrolysis as described above was carried out using standard bench scale evaporative crystallizer.

[00199] The crystallizer body was a 3 L cylindrical stainless steel (SS) vessel with a hemispherical bottom and was heated with a 100 watt external SS mantle. The vessel was equipped with a variable speed overhead agitator. The liquor temperature

inside the crystallizer was maintained at 80°C by operating under vacuum, using a two stage rotary vane vacuum pump downstream of the condenser. A needle valve was used to bleed atmospheric air into the vacuum line to control the internal pressure. A digital pressure gauge displays the absolute pressure for the system for operator interface. The temperature of the saturated vapour was calculated and was used to calculate the boiling point rise (BPR) of the solution.

[00200] The crystallizer was operated in a quasi-steady state manner, with continuous feed and evaporation and batch slurry removal. Slurry was removed batch-wise and separated through a laboratory 5 inch vertical basket centrifuge with a 10-15 micron screen. The LiOH.H₂O product was dried in a glove box (Veolia™). Nitrogen was used in the crystallizer operation in order to minimize CO₂ contamination including the feed tank, the crystallizer body during standby, centrifuge during solid-liquid separation, and the glove box drying operation. The catholyte LiOH from the electrolysis had the composition set out in the table below.

Table 10

Analytical Parameters	Units	Feed Analysis
pH	pH Unit	13.10
Density	g/cm ³	1.089
Total Solids	% w/w	10.10
Al	ppm	<1
Sb	ppm	<1
As	ppm	<10
Ba	ppm	<1
Be	ppm	<1
B	ppm	1
Cd	ppm	<1
Ca	ppm	<1
Cl	ppm	325
Cr	ppm	<1
Co	ppm	<1
Cu	ppm	<1
OH	% w/w	6.98
Fe	ppm	<1
Pb	ppm	<1
Li	% w/w	2.76

Mg	ppm	3
Mn	ppm	<1
Mo	ppm	<1
Ni	ppm	<1
P	ppm	<10
K	ppm	<10
Se	ppm	<10
Si	ppm	5
Ag	ppm	<1
Na	ppm	<10
Sr	ppm	<1
Th	ppm	<1
Total Inorganic Carbon	ppm as C	32
Sn	ppm	<10
Ti	ppm	<1
Va	ppm	<1
Zn	ppm	<1

[00201] The above described catholyte was subjected to double crystallization, again as described above. The solids were centrifuged, washed thoroughly to reduce further the concentration of impurities, and dried in vacuum at low temperature ~ 50°C.

[00202] This demonstrates that impurities such as Cl, K and Na remain soluble in the mother liquor, and are eliminated from the LiOH.H₂O crystals to what is understood to be an acceptable level. The dried LiOH.H₂O crystals have a composition as set out in the table below.

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Table 11

Analytical Parameters	Units	Crystal DI Washed
LiOH	% w/w	56.6
Al	ppm	1
Sb	ppm	<1
As	ppm	<10
Ba	ppm	<1
Be	ppm	<1
B	ppm	<1
Cd	ppm	1
Ca	ppm	<1
Cl	ppm	24
Cr	ppm	<1
Co	ppm	<1
Cu	ppm	2
OH	% w/w	39.4
Fe	ppm	1
Pb	ppm	<1
Li	% w/w	16.4
Mg	ppm	1
Mn	ppm	<1
Mo	ppm	<1
Ni	ppm	1
P	ppm	<10
K	ppm	<10
Se	ppm	<10
Si	ppm	19
Ag	ppm	<1
Na	ppm	<10
Sr	ppm	<1
S	ppm	<10
Th	ppm	<1
Total Inorganic C	ppm as C	343
Sn	ppm	<10
Ti	ppm	<1
Va	ppm	<1
Zn	ppm	<1

[00203] It is particularly envisaged that the first and/or second purification steps may comprise more than a single stage, pass or repeat of contact or exposure between the lithium containing solution passed to them and the adsorbent or graphene based filter medium, respectively, to realise the most significant benefits of the combination process of the present invention.

[00204] As can be seen with reference to the above description, a particular advantage is realised in accordance with the present invention in that the nanotube/fibre adsorbents of the present invention can be readily separated from a liquid after the sorption by filtration, sedimentation, or centrifugation because of their fibril morphology. It is expected that this will significantly reduce the cost of separation of the adsorbent from the liquid.

[00205] As can further be seen with reference to the above description, in one form the present invention provides a process to separate and purify LiCl and reduce or eliminate impurities in LiCl solutions to concentrations acceptable for use as a feed to an electrolysis step for the production of lithium hydroxide. In turn, such may be used as a pre-cursor in high purity applications such as lithium ion batteries. This purification is achieved as described hereinabove.

[00206] The preferred process according to the present invention specifically provides a method of reducing the contaminant impurities in the LiCl solution to less than about 20 ppm.

[00207] In one form, the combination of the techniques of adsorption and filtration using a graphene filter medium is particularly advantageous in the production of substantially purified lithium solutions, particularly lithium chloride solutions. One basis for this apparent synergy in the combination of the adsorption and filtration appears to be the effectiveness of adsorption in removing sodium ions, in particular, which in turn ensures that the part-purified lithium containing solution that is then passed to the graphene based filter medium is able to be further purified effectively thereby.

[00208] Again with reference to the above description, the present invention provides an improved extraction method for the extraction of lithium from a LiCl containing brine. Preferred processes according to the present invention are envisaged as being able to meet the needs and demands of today's lithium ion battery industry. Preferred processes according to the present invention specifically provide a method of reducing the contaminant impurities in the brine to less than 20 ppm.

[00209] Modifications and variations such as would be apparent to the skilled addressee are considered to fall within the scope of the present invention.

Claims

1. A combined processing method for the purification of lithium containing solutions, the method comprising the method steps of:
 - a) passing a lithium containing solution to one or more purification steps to produce a substantially purified lithium chloride solution; and
 - b) passing the substantially purified lithium chloride solution of step a) to an electrolysis step in which lithium hydroxide monohydrate is produced,wherein the one or more purification steps comprises either or both of a first purification step in which the lithium containing solution is contacted with a titanate adsorbent whereby lithium ions are adsorbed thereon whilst rejecting substantially all other cations, the recovery of lithium from the adsorbent providing a part-purified lithium containing solution, and a second purification step in which a graphene based filter medium is utilised to provide a further purified lithium containing solution.
2. The method of claim 1, wherein the lithium containing solution is a lithium containing brine.
3. The method of claim 1 or 2, wherein the adsorbent is provided in the form of either a hydrated titanium dioxide or a sodium titanate.
4. The method of claim 3, wherein the hydrated titanium dioxide is produced from titanium dioxide.
5. The method of any one of the preceding claims, wherein the further purified lithium containing solution is a substantially pure lithium chloride solution.
6. The method of any one of the preceding claims, wherein the brine contains impurities from the group of sodium, potassium, magnesium, calcium and borate.

7. The method of claim 6, wherein the impurity concentration of the substantially pure lithium chloride solution does not exceed about 20 ppm.
8. The method of any one of claims 2 to 7, wherein the brine contains lithium in the range of about 500 to 1500 ppm, and impurities including magnesium in the range of about 0.15% to 0.30%, calcium in the range of about 0.05% to 0.1%, sodium in the range of about 8 to 10%, potassium in the range of about 0.7% to 1.0%, and borate in the range of about 0.15% to 0.20%.
9. The method of claim 8, wherein the brine contains about 700 ppm lithium, about 0.19% magnesium, about 0.09% calcium, about 8.8% sodium, about 0.8% potassium and about 0.18% borate.
10. The method of any one of claims 2 to 9, wherein the brine solution is adjusted to a pH of 7 through the addition of a base.
11. The method of claim 10, wherein the base is provided in the form of sodium hydroxide.
12. The method of any one of the preceding claims, wherein the contact between the lithium containing solution and the adsorbent preferably takes place at or about room or ambient temperature.
13. The method of any one of claims 2 to 12, wherein the brine is collected into a vessel and cooled to room temperature prior to its exposure to the adsorbent.
14. The method of any one of the preceding claims, wherein the contact or residence time between the brine solution and the adsorbent is between about 4 to 24 hours.
15. The method of claim 14, wherein the contact or residence time between the brine solution and the adsorbent is:
 - a) between about 8 to 24 hours;
 - b) between about 20 to 24 hours; or

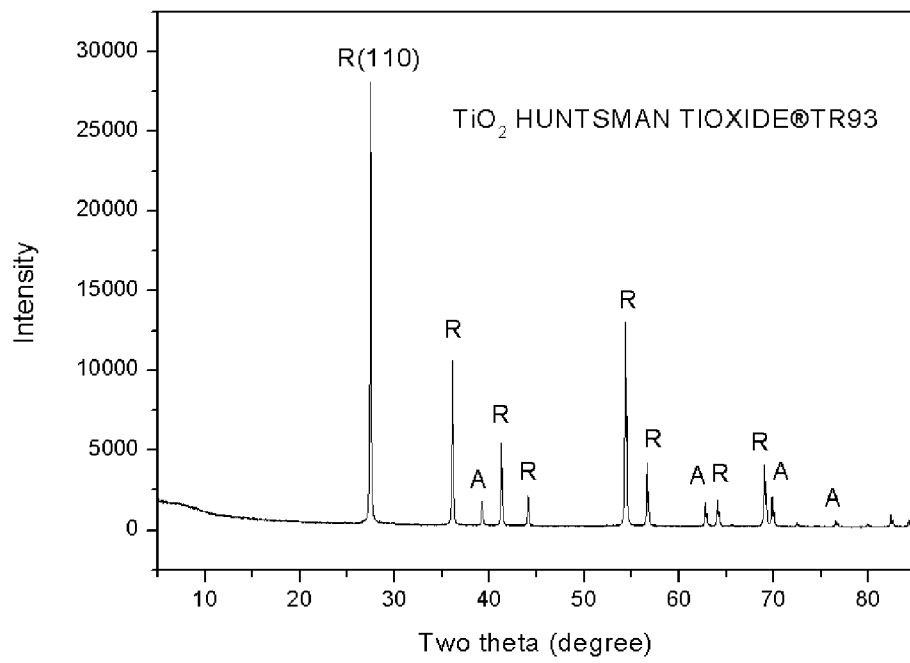
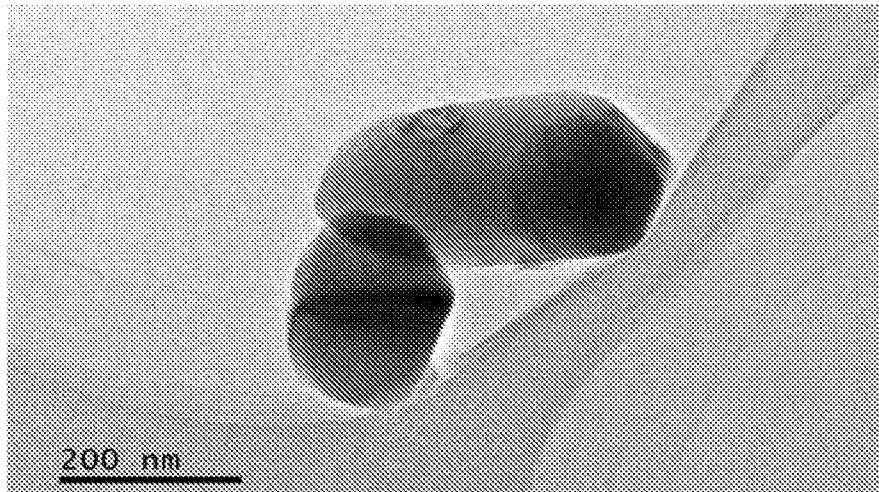
c) between about 8 to 16 hours.

16. The method of any one of the preceding claims, wherein the recovery of lithium from the adsorbent is achieved through the regeneration of the adsorbent by the addition of an acid solution and the adsorbed lithium is extracted to provide the part purified lithium containing solution.
17. The method of claim 16, wherein the acid solution is a solution of hydrochloric acid.
18. The method of claim 17, wherein the amount of lithium extracted from the adsorbent through exposure to the acid solution is greater than about 90%.
19. The method of claim 18, wherein the amount of lithium extracted from the adsorbent through exposure to the acid solution is about 100% of the adsorbed lithium.
20. The method of any one of the preceding claims, wherein the graphene based filter medium of the second purification step preferably comprises a graphene membrane formed of one or more graphene, graphene oxide and/or reduced graphene oxide and to which the part-purified lithium containing solution is presented.
21. The method of claim 20, wherein the passing of the part purified lithium containing solution to the second purification step produces a filtrate or permeate that is enriched in relative terms in lithium ions, providing the further purified lithium containing solution.
22. The method of claim 20 or 21, wherein the second purification step is conducted under pressure.
23. The method of claim 22, wherein the pressure is at or about 10 bar.
24. The method of any one of the preceding claims, wherein the further purified lithium containing solution is suitable for use in the production of battery grade lithium chemicals.
25. The method of any one of the preceding claims, wherein the graphene is provided as a graphene oxide membrane formed in turn from graphite oxide powder.

26. The method of claim 25, wherein the graphene oxide membrane is supported on a first support that is in turn located in an aperture of a second support.
27. The method of claim 26, wherein the first support is an anodic alumina disc.
28. The method of claim 26 or 27, wherein the second support is a copper plate.
29. The method of any one of claims 20 to 28, wherein the graphene oxide membrane is reduced by way of exposure to ascorbic acid.
30. The method of any one of claims 20 to 29, wherein the area used for pressure filtration is about 1 – 2 cm².
31. The method of any one of claims 20 to 30, wherein the membrane is supported by a porous substrate.
32. The method of claim 31, wherein the porous substrate is provided in the form of polyether sulfone.
33. The method of claim 31 or 32, wherein an adhesive material is applied to the porous substrate to increase the bond between the substrate and the graphene material.
34. The method of claim 33, wherein the adhesive material is provided in the form of a polymer.
35. The method of claim 34, wherein the polymer is a positively charged polymer.
36. The method of claim 35, wherein the positively charged polymer is polydiallyldimethylammonium chloride.
37. The method of any one of claims 20 to 36, wherein the graphene membrane has a thickness of between 30 to 200 nm.
38. The method of any one of claims 20 to 37, wherein the thickness of the graphene membrane is between 150 to 200 nm.

39. The method of any one of the preceding claims, wherein the level of salt rejection achieved by the second purification step is 20% or greater as measured by the conductivity of a permeate relative to that of the part-purified lithium containing solution.
40. The method of claim 39, wherein lithium is the least rejected ion or salt of the second purification step.
41. The method of any one of the preceding claims, wherein the first and second purification steps comprise one or more stages, passes or repeats of contact or exposure between the lithium containing solution passed to them and the adsorbent or filter medium, respectively.
42. The method of any one of the preceding claims, wherein the part-purified lithium containing solution produced in the first purification step is passed in whole or part to the second purification step.
43. The method of any one of the preceding claims, wherein the electrolysis step is conducted by passing the substantially purified lithium solution to one or more electrolytic cells or electrolyzers to convert the lithium present to lithium hydroxide.
44. The method of claim 43, wherein substantially only lithium chloride and water are consumed in the electrolysis step, thereby producing substantially only lithium hydroxide, chlorine and hydrogen as products.
45. The method of claim 43 or 44, wherein between 6 to 20 electrolyzers are provided.
46. The method of claim 44 or 45, wherein the chlorine and hydrogen so produced are combined to produce HCl acid.
47. The method of any one of claims 43 to 46, wherein the electrolysis step is conducted using chlor-alkali technology at about or less than 50°C and a current efficiency of greater than about 70%.

48. The method of any one of the preceding claims, wherein the lithium hydroxide product produced in the electrolysis step is passed to a crystallisation step in which lithium hydroxide monohydrate is crystallised.

**Figure 1****Figure 2**

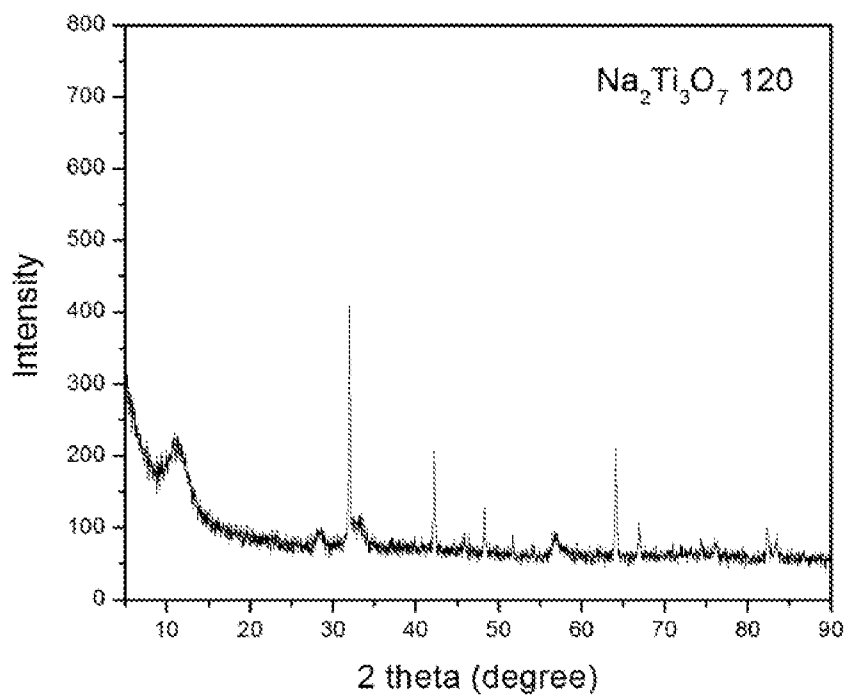


Figure 3

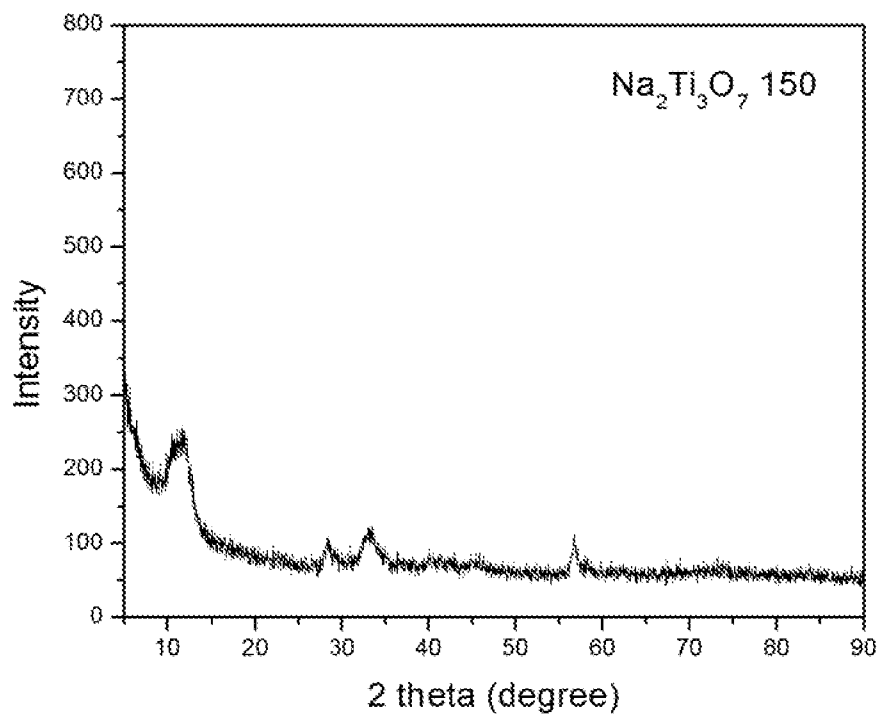


Figure 4

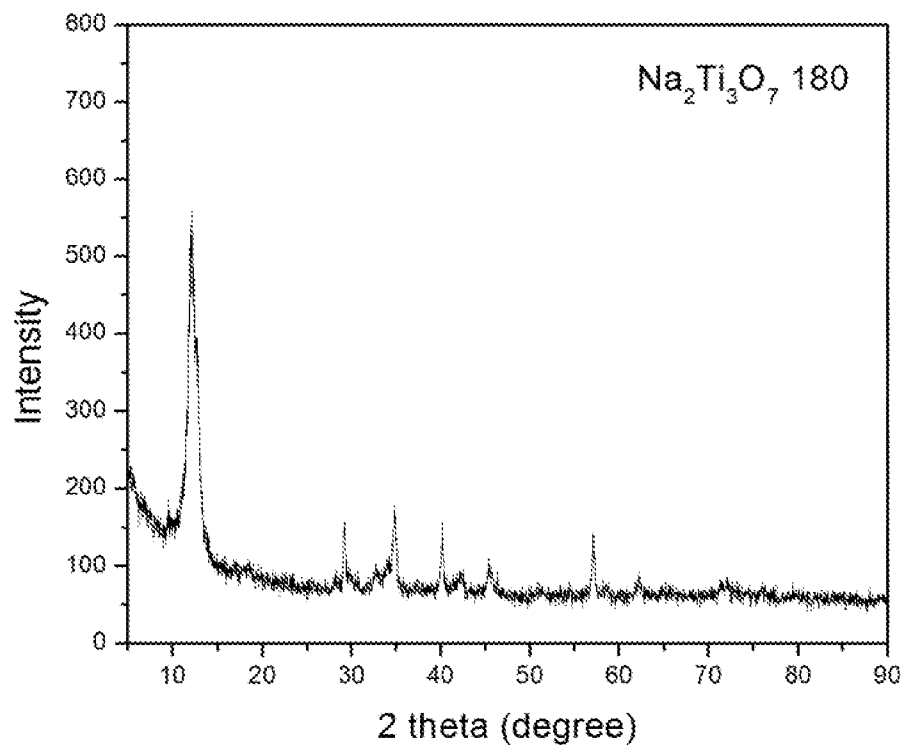


Figure 5

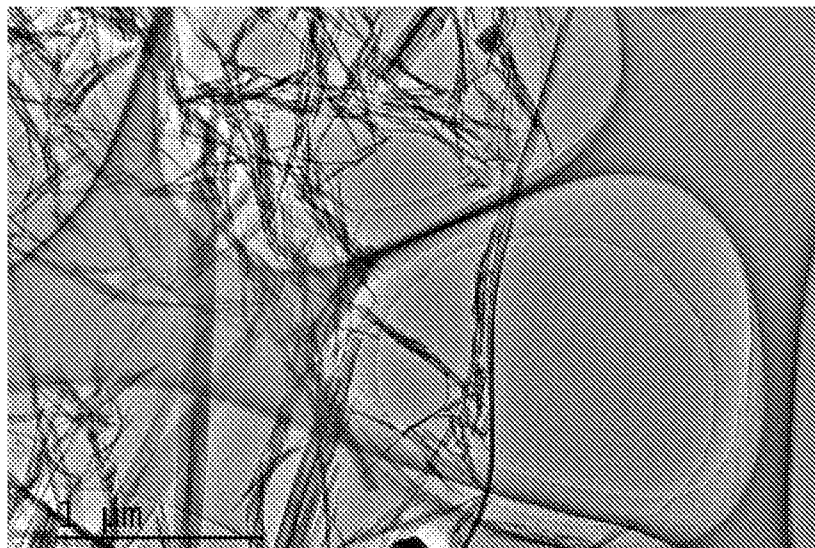


Figure 6

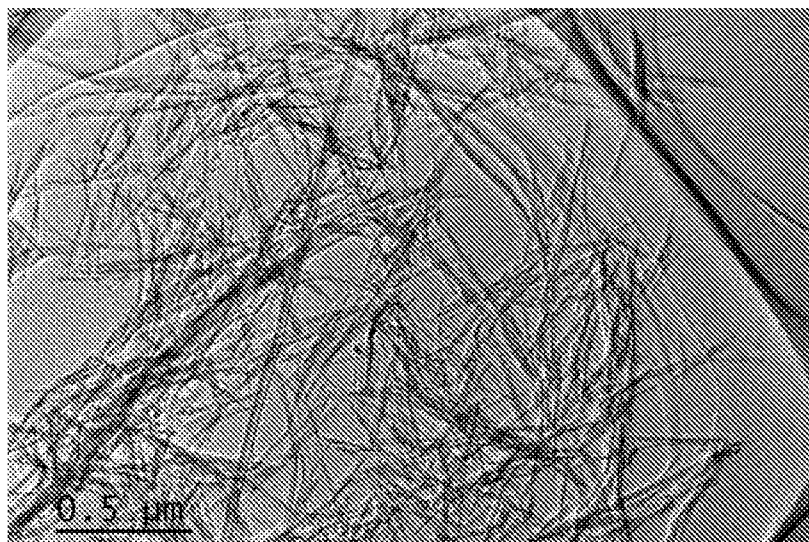


Figure 7

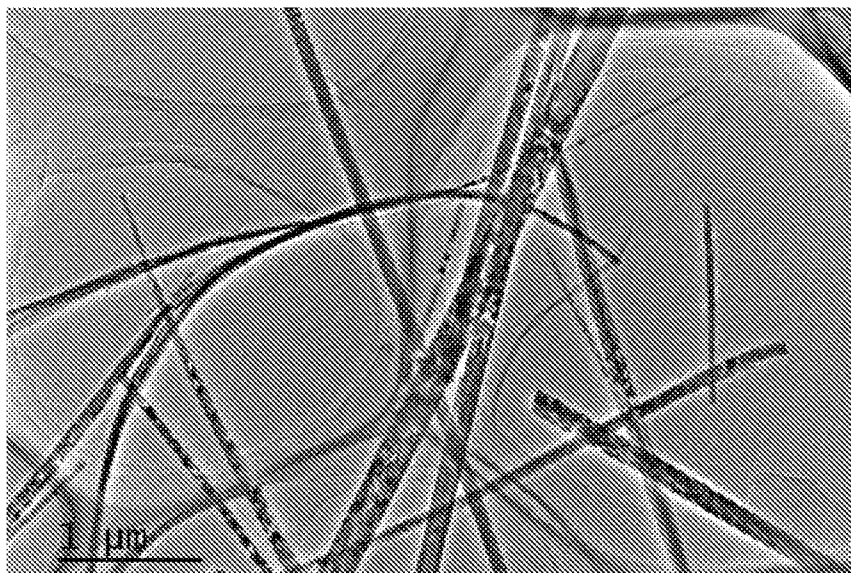


Figure 8

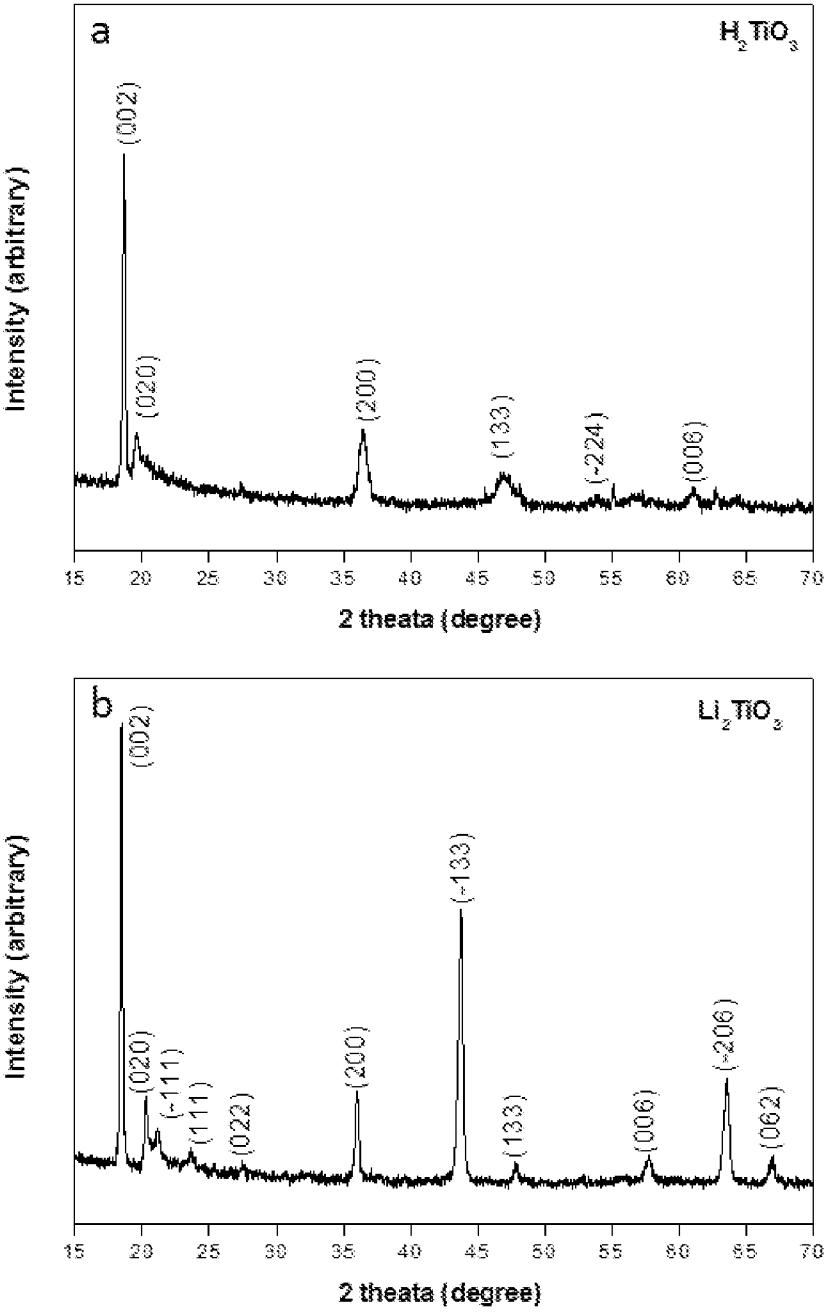


Figure 9

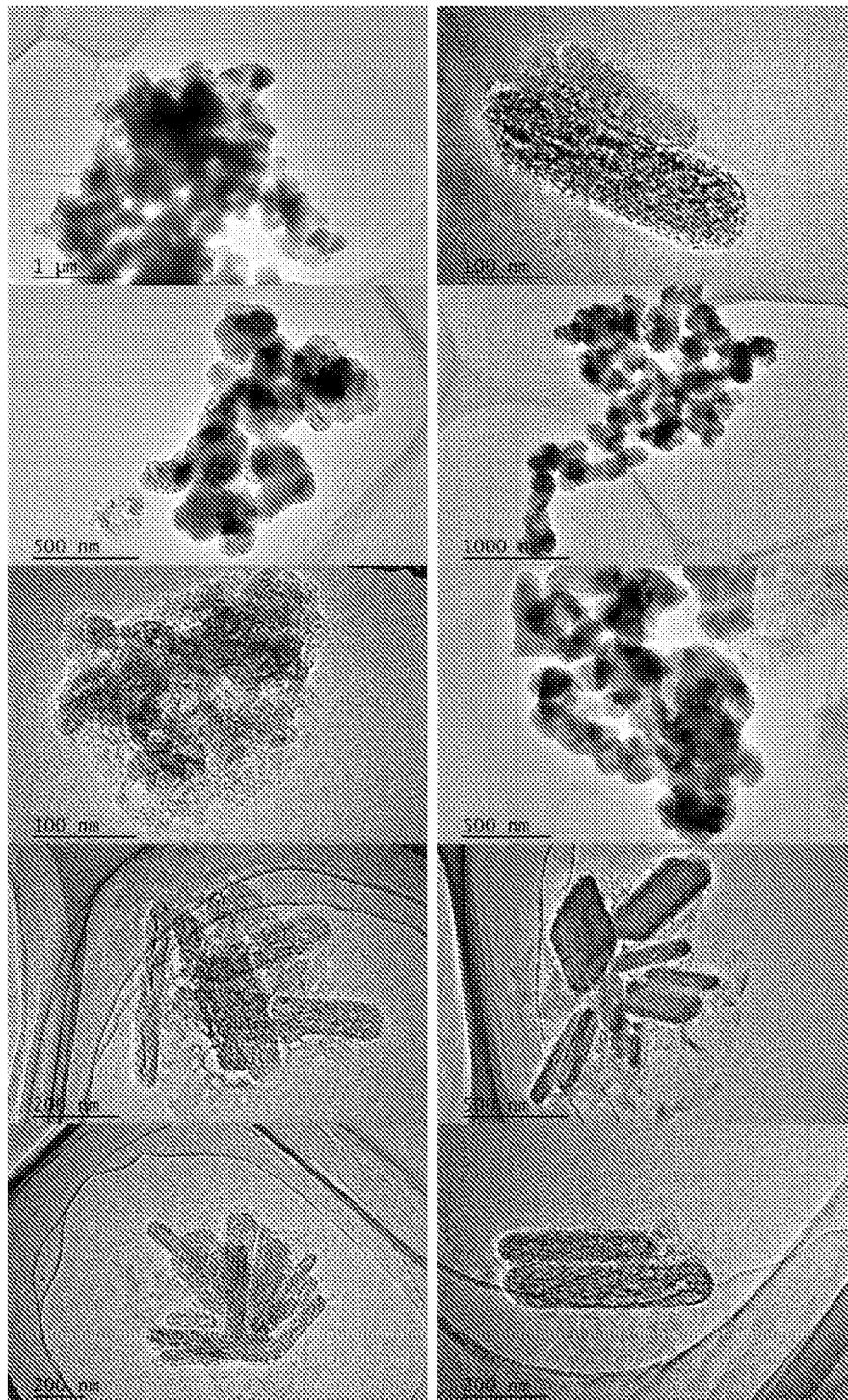


Figure 10

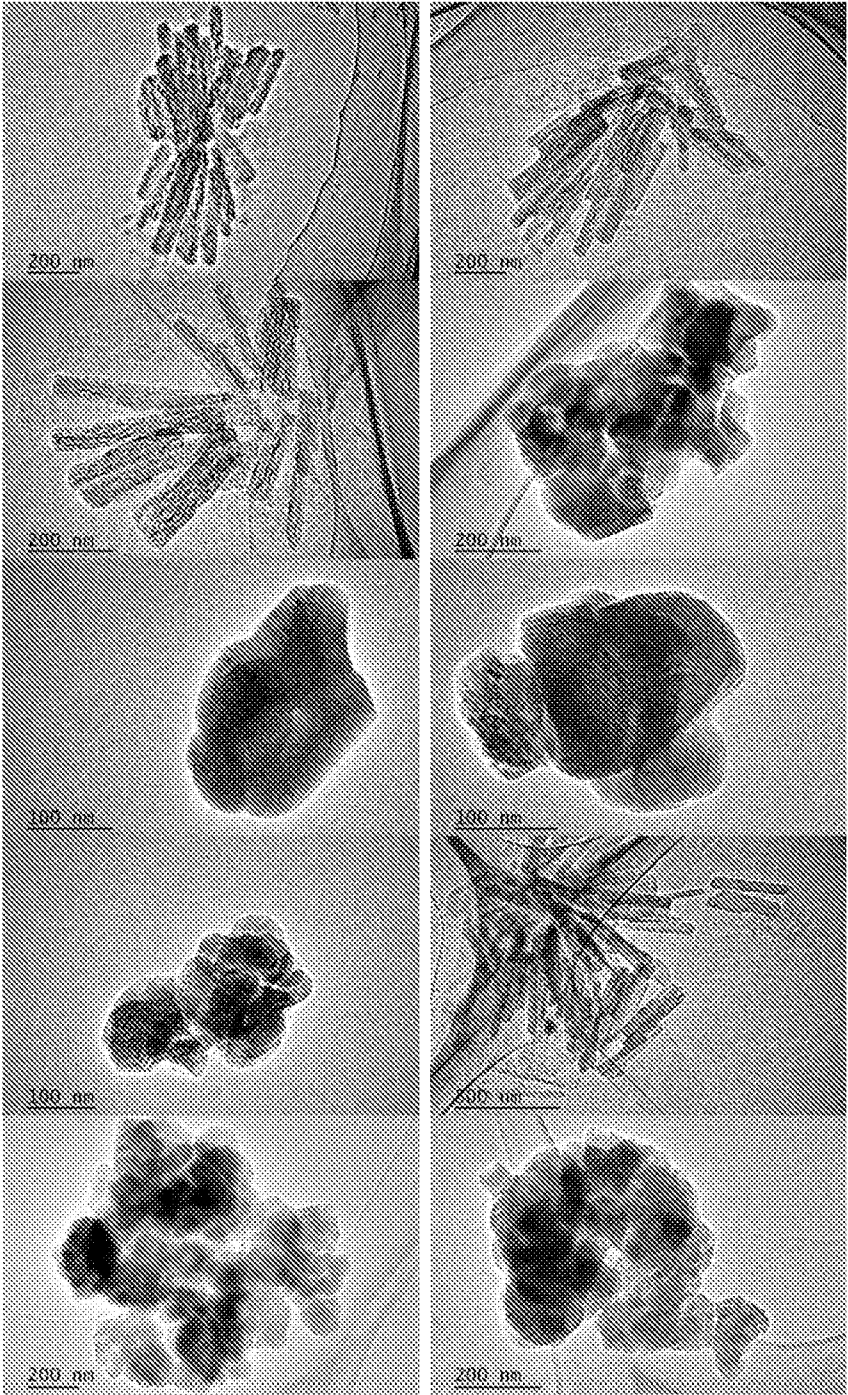


Figure 11

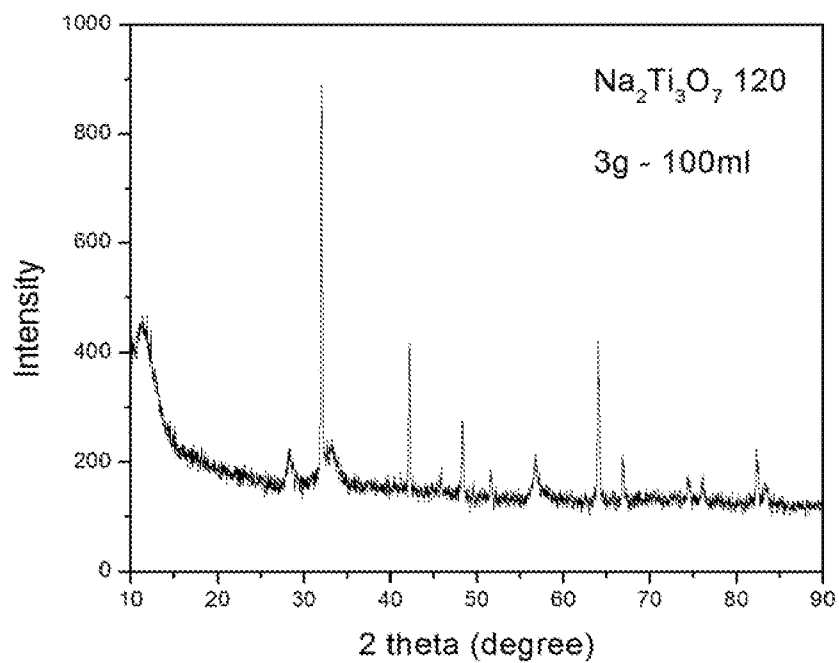


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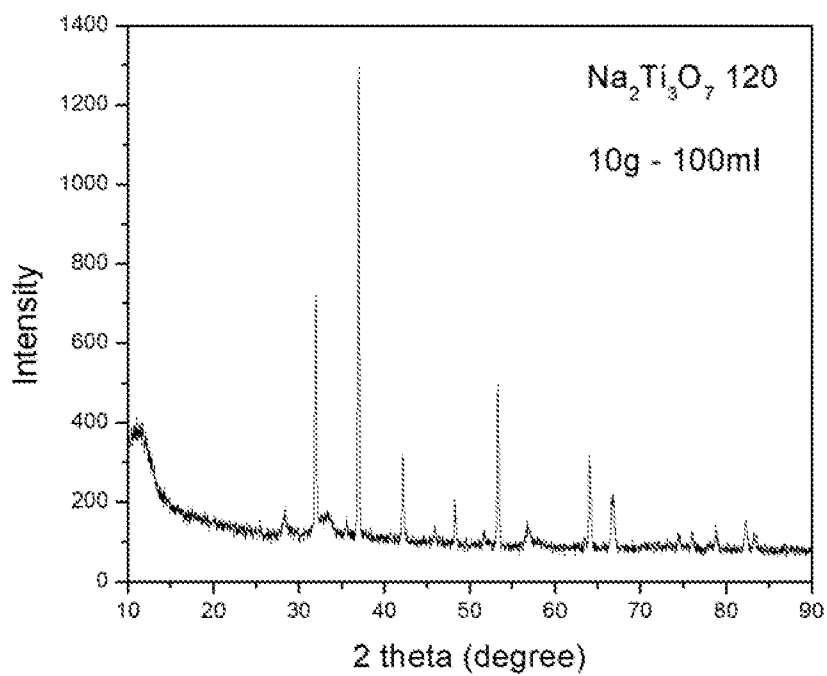


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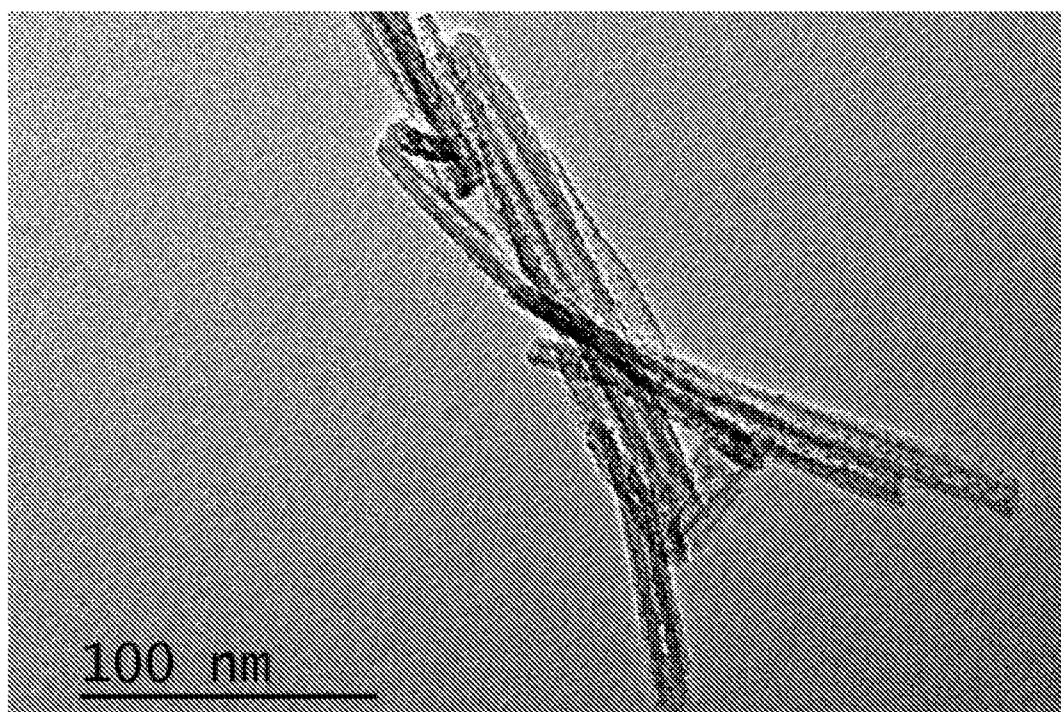
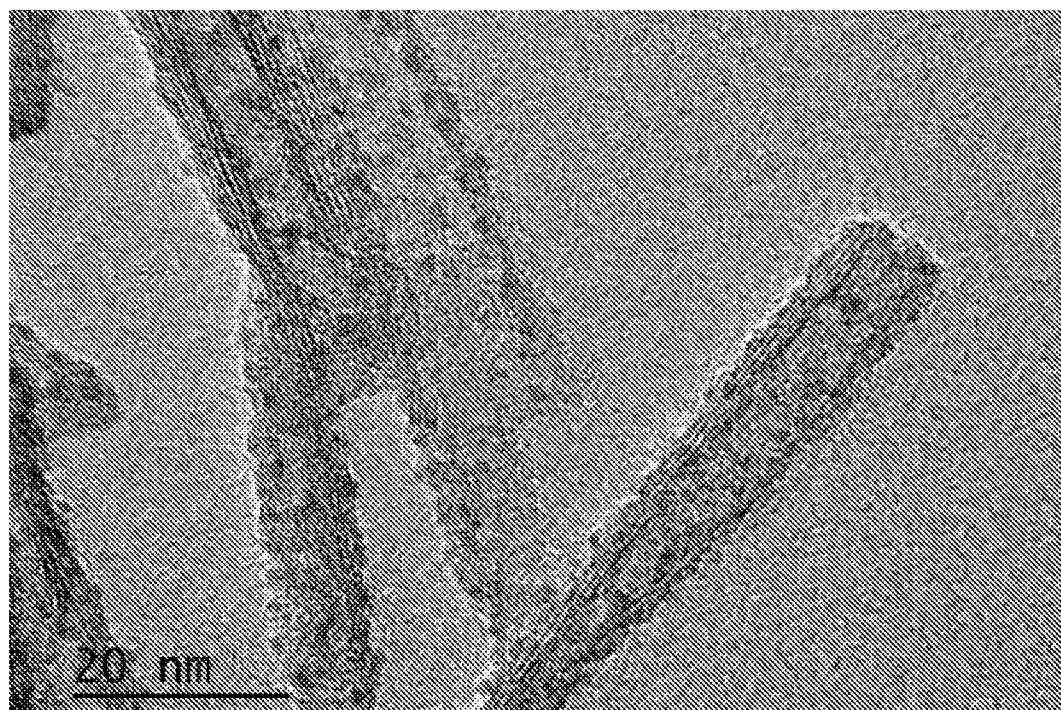


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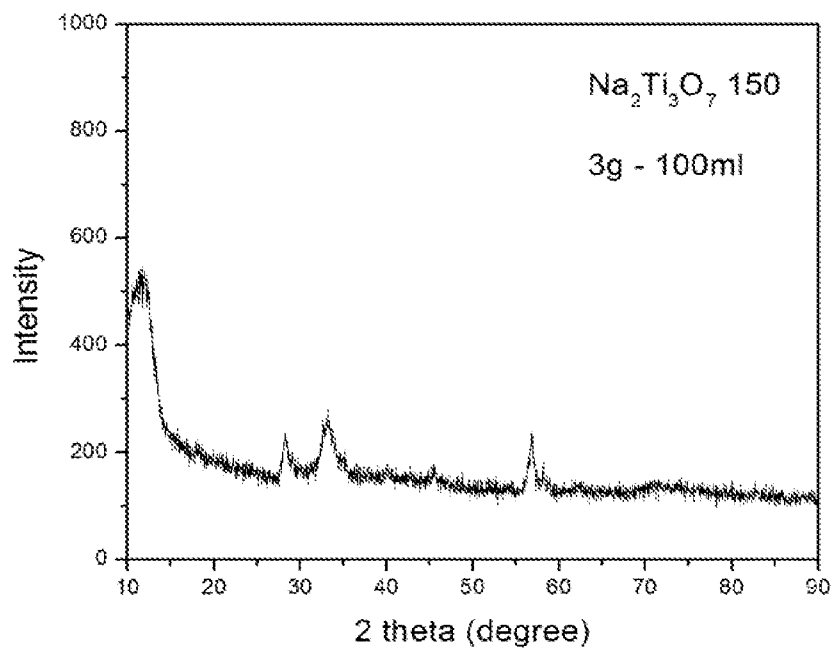


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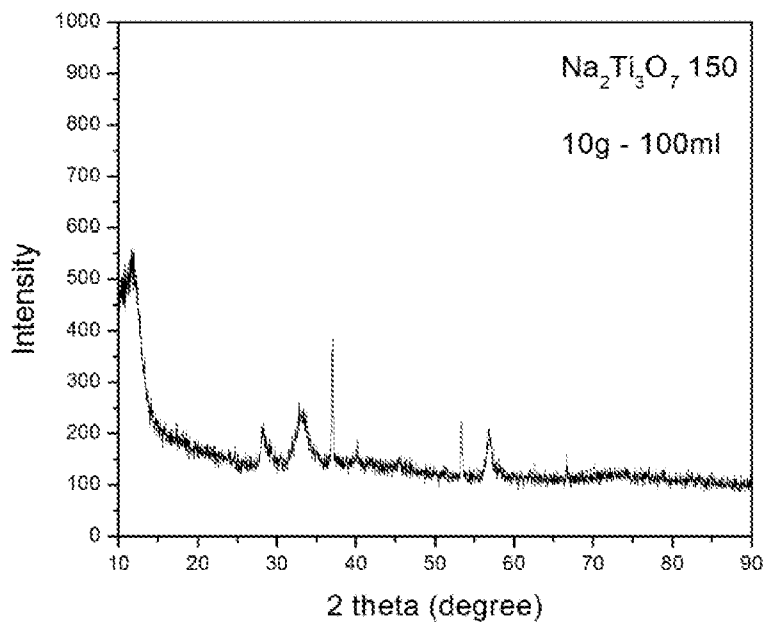


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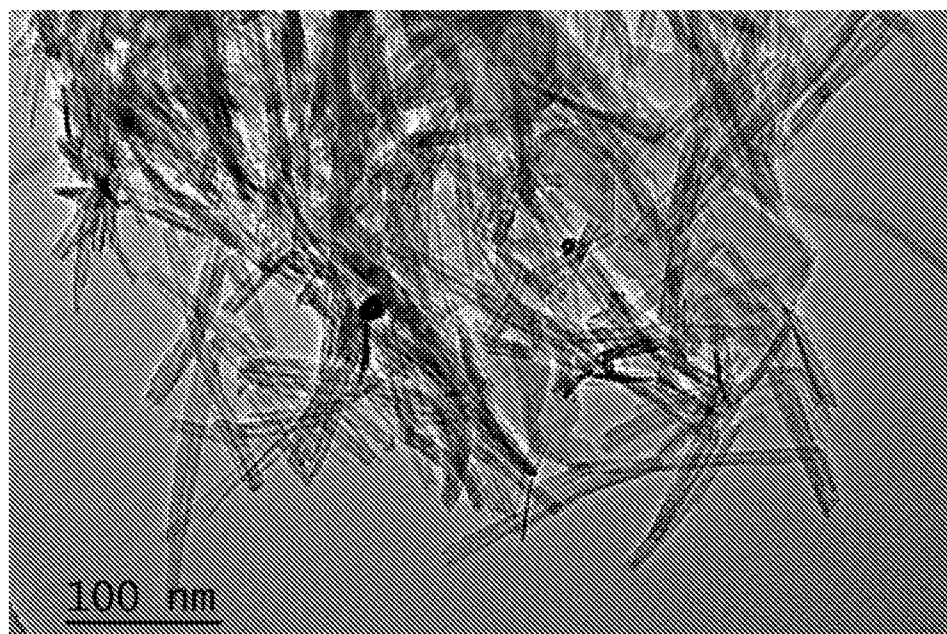
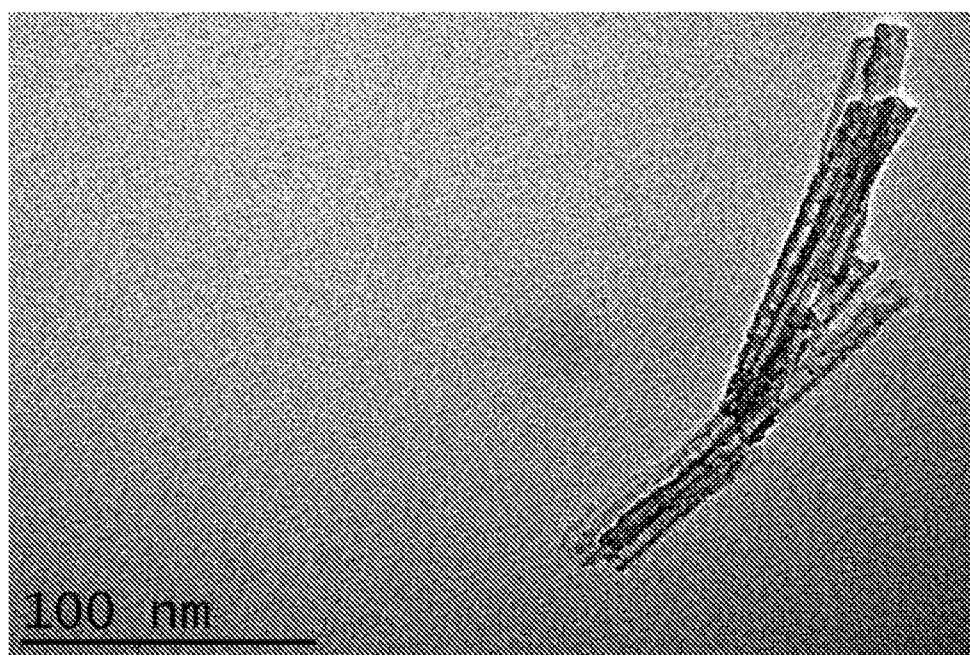


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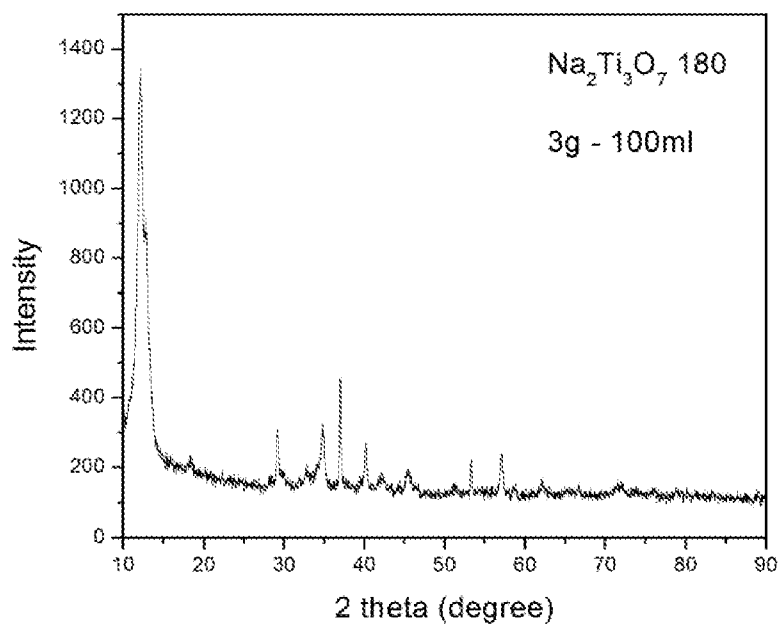


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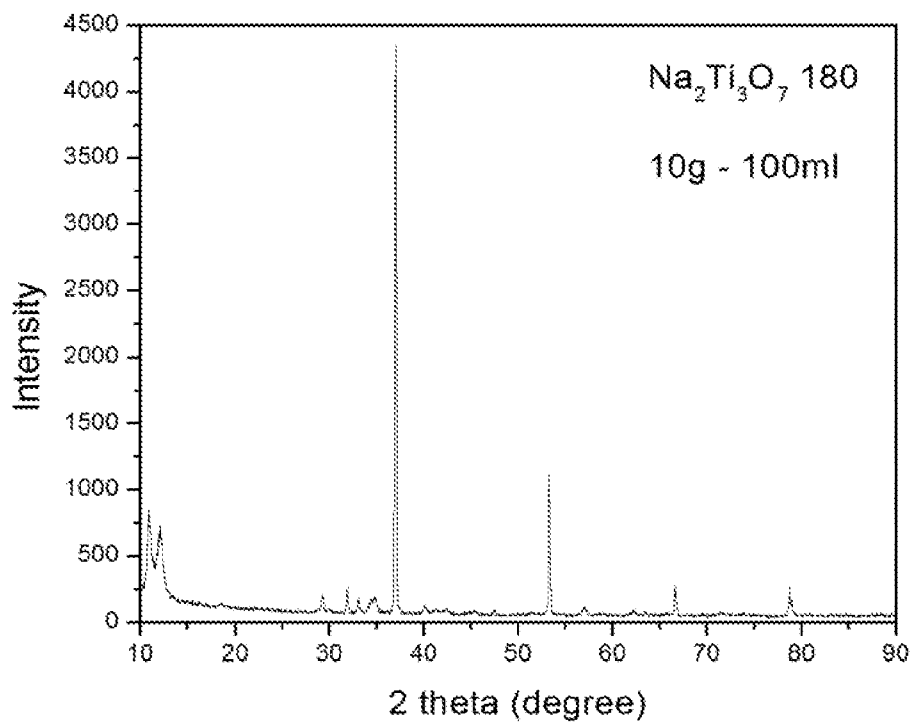


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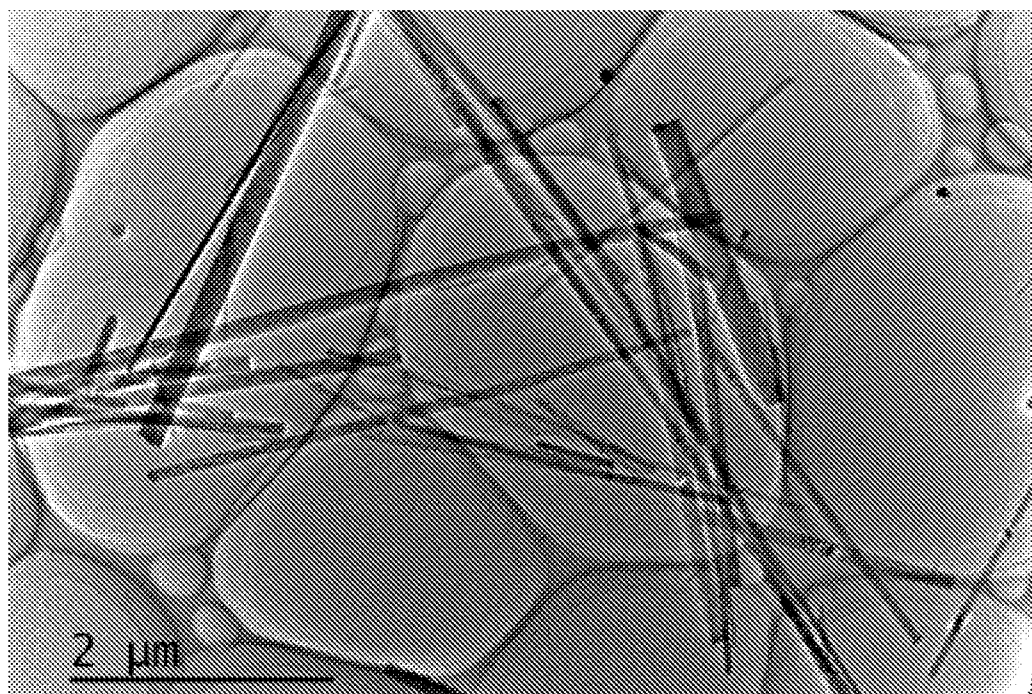
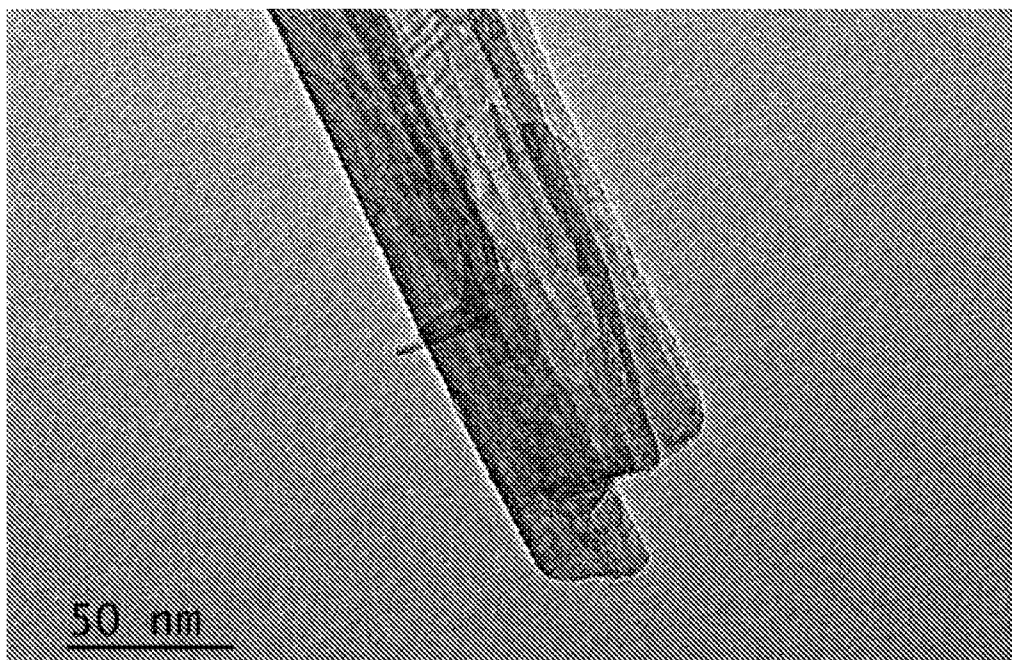


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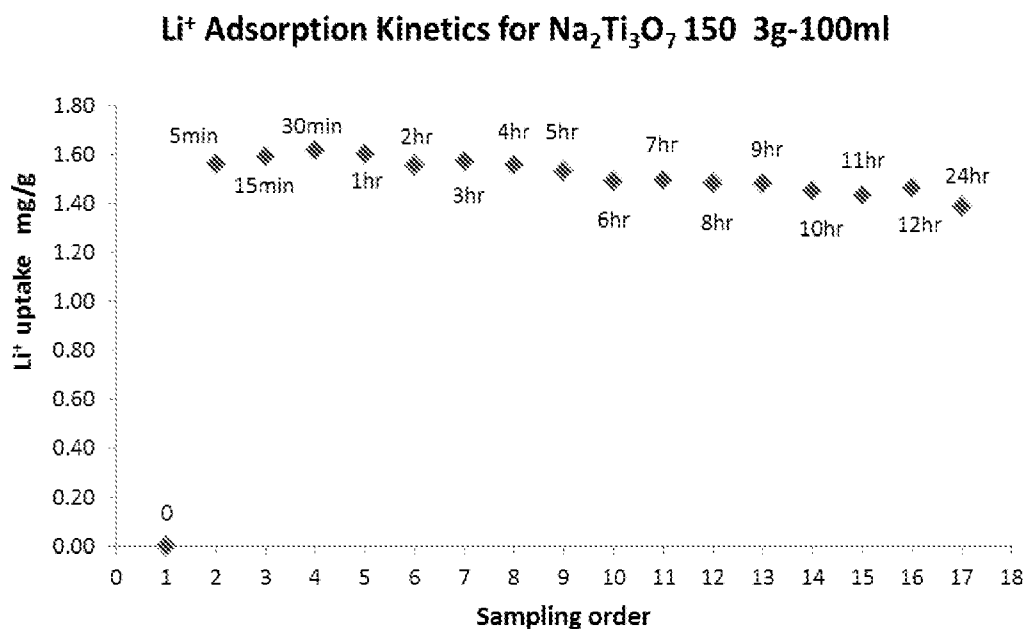


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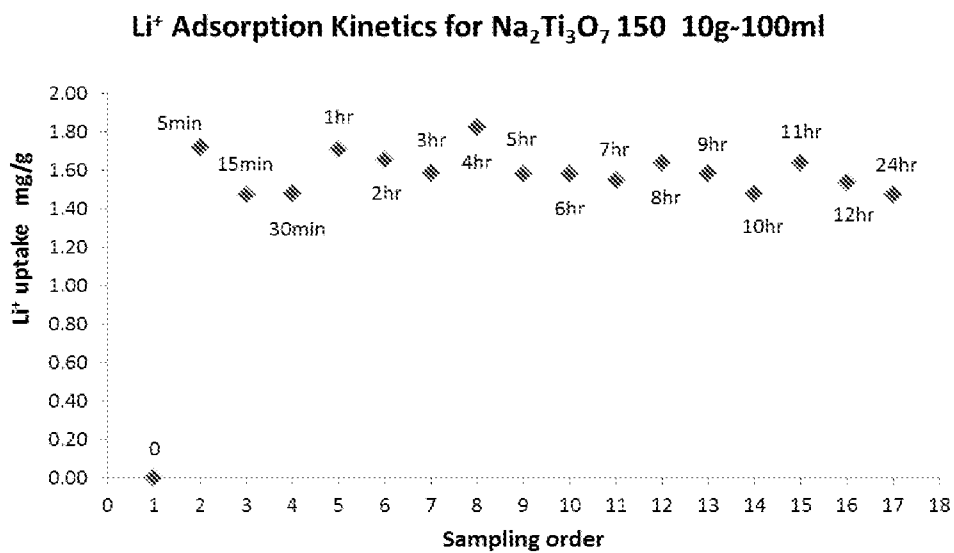


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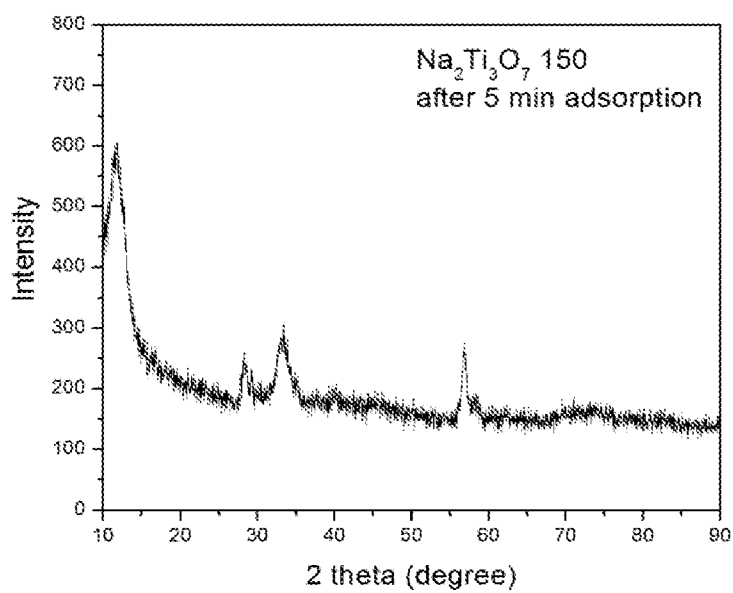


Figure 23 (a)

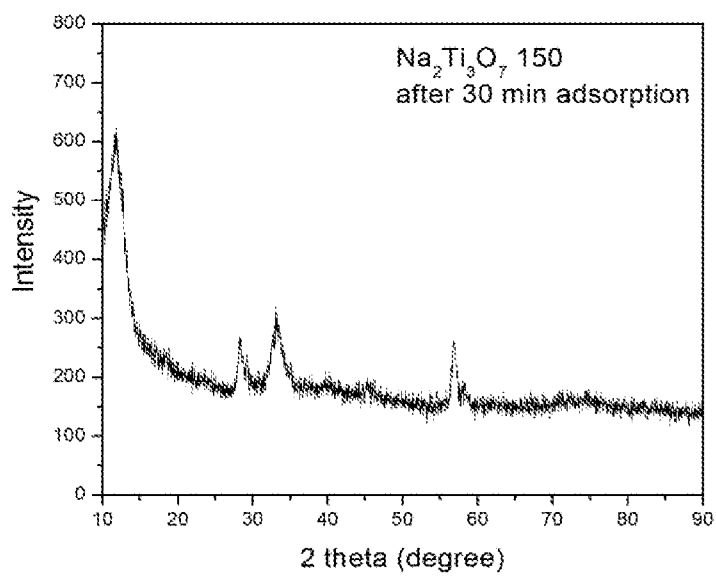


Figure 23 (b)

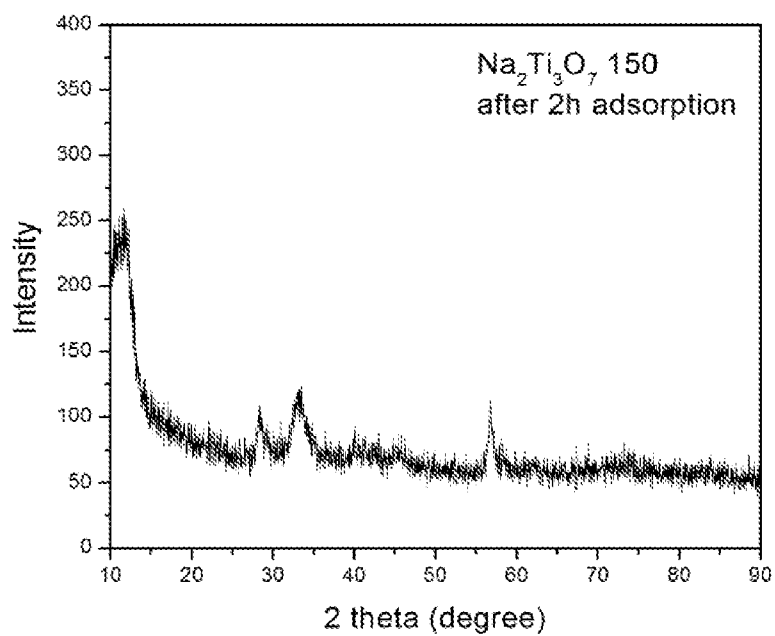


Figure 23 (c)

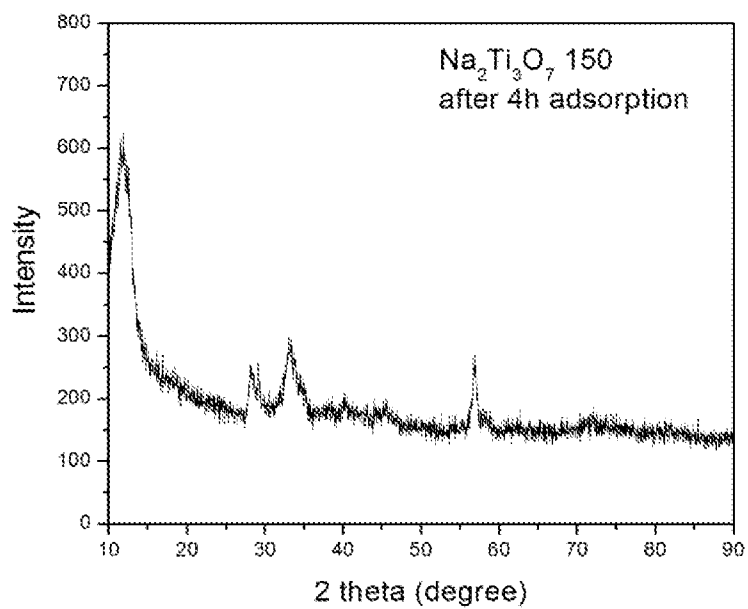


Figure 23 (d)

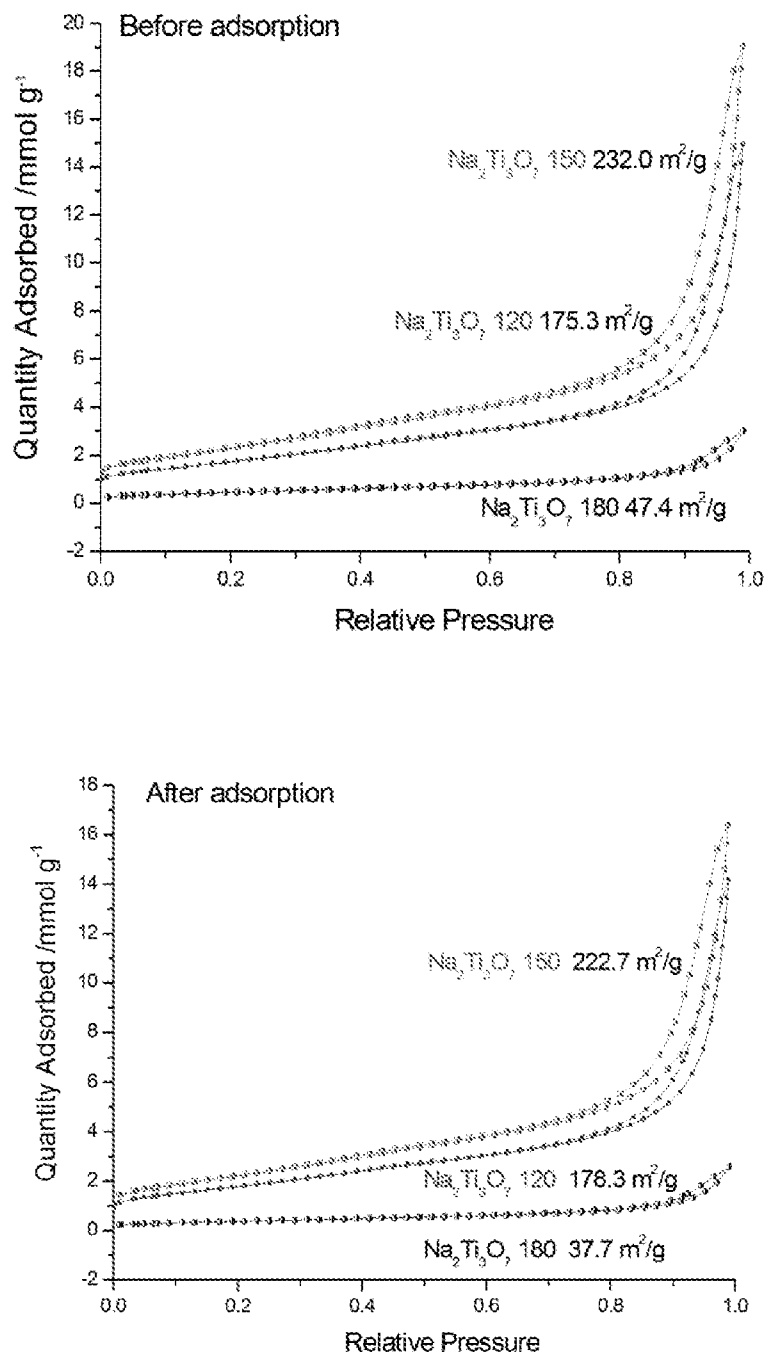
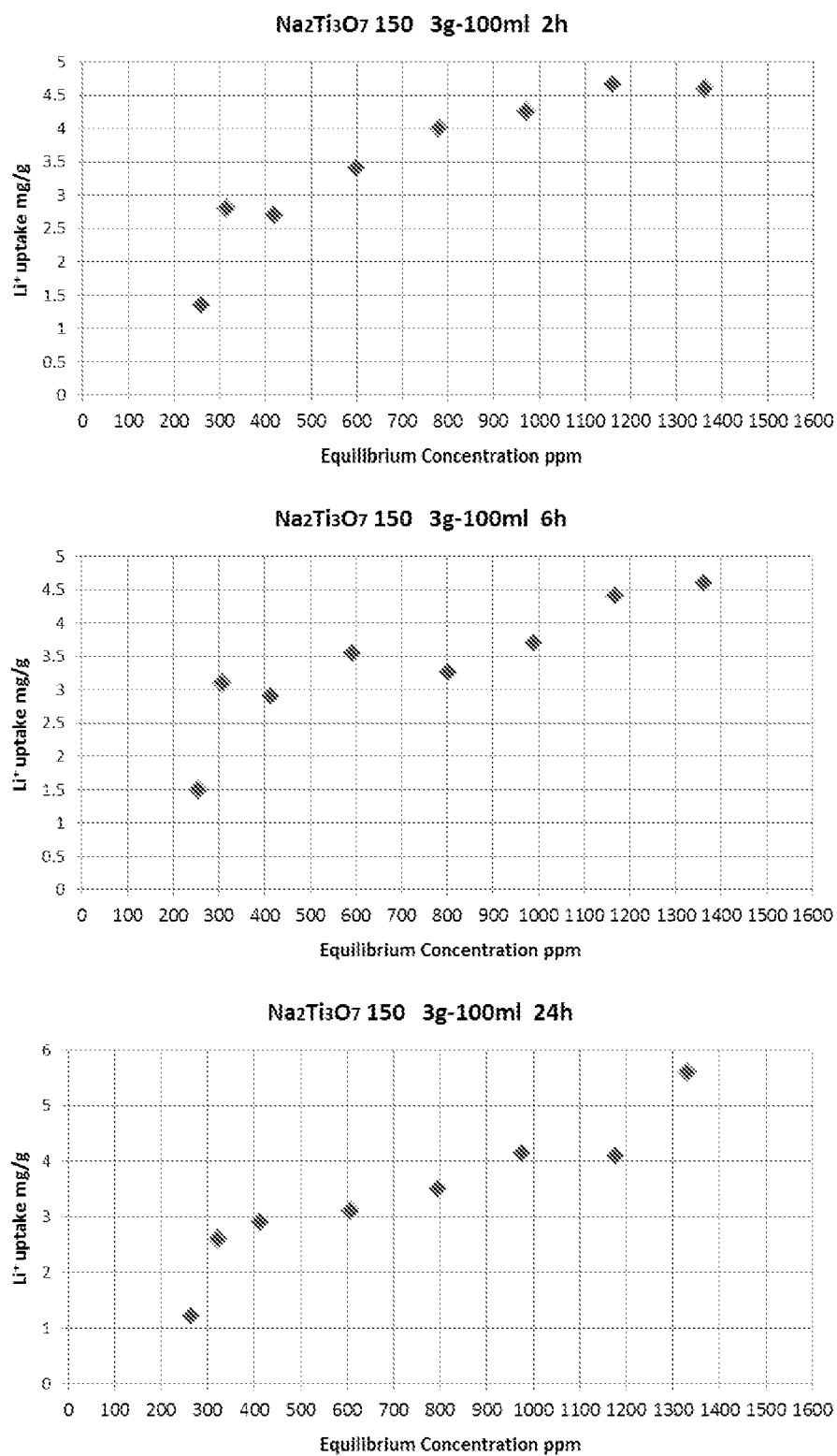


Figure 24

**Figure 25**

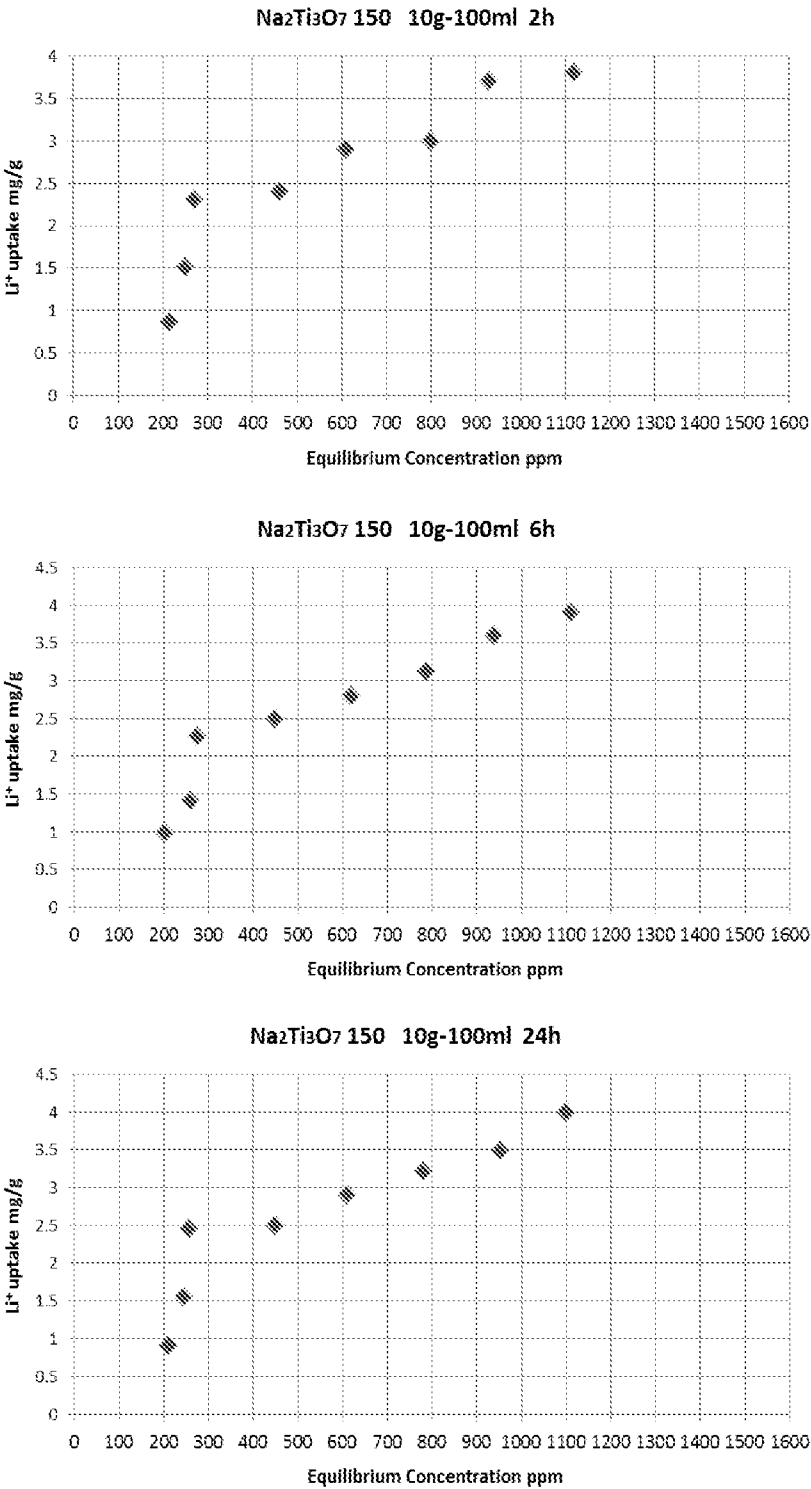


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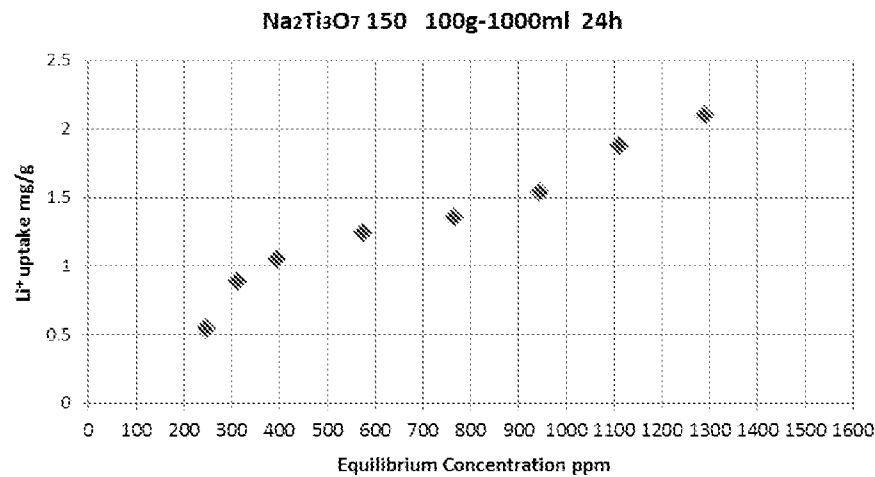


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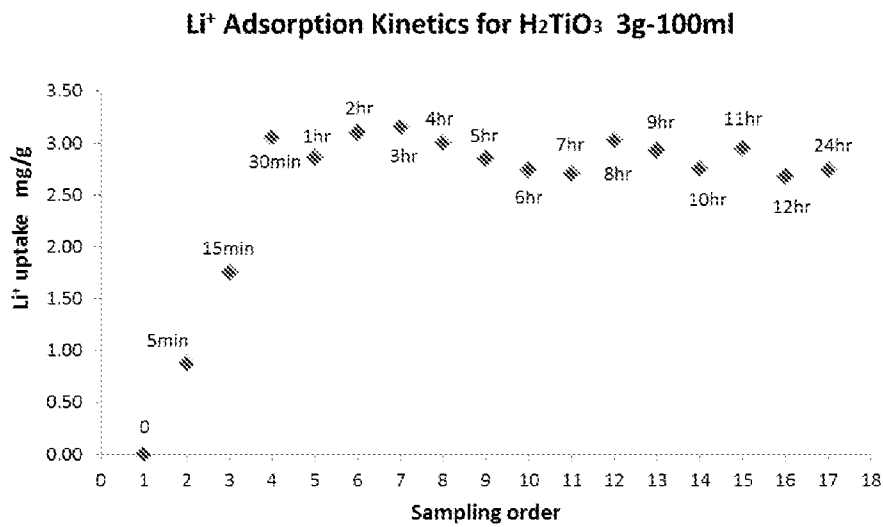


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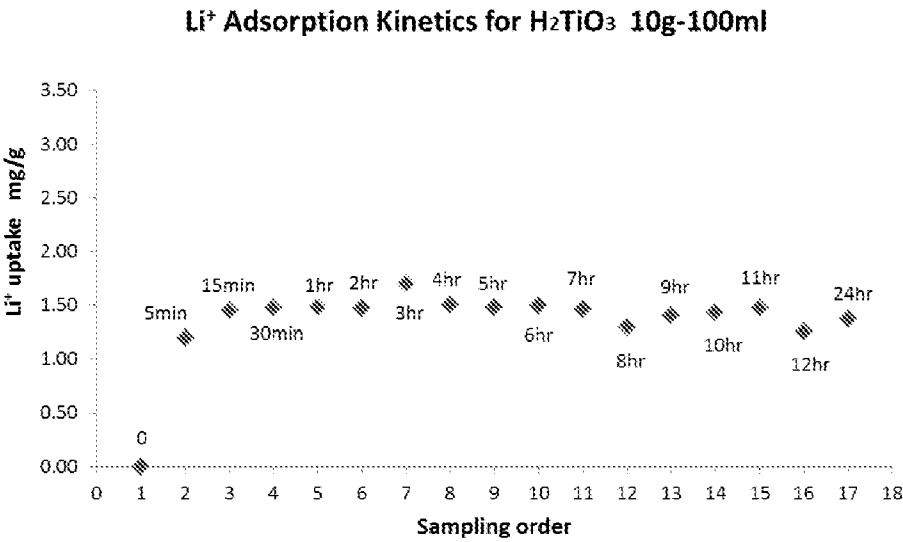


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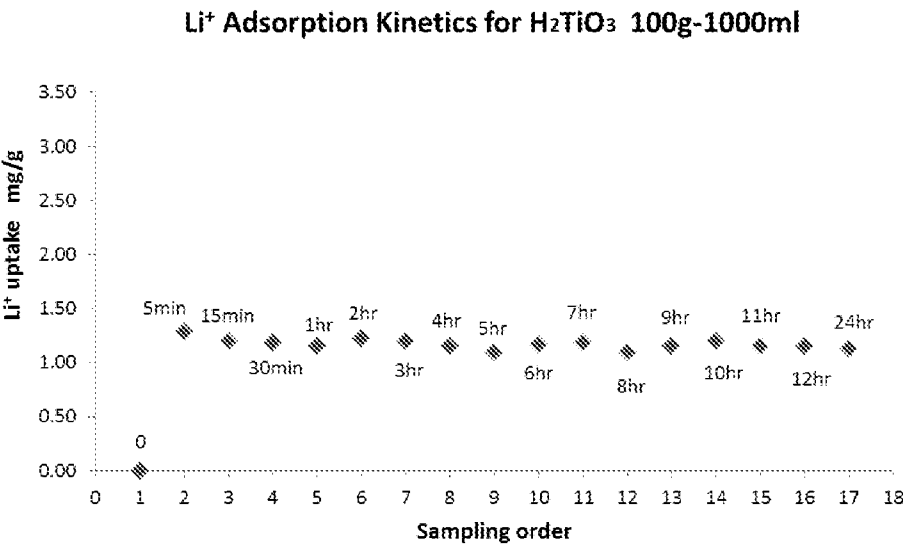


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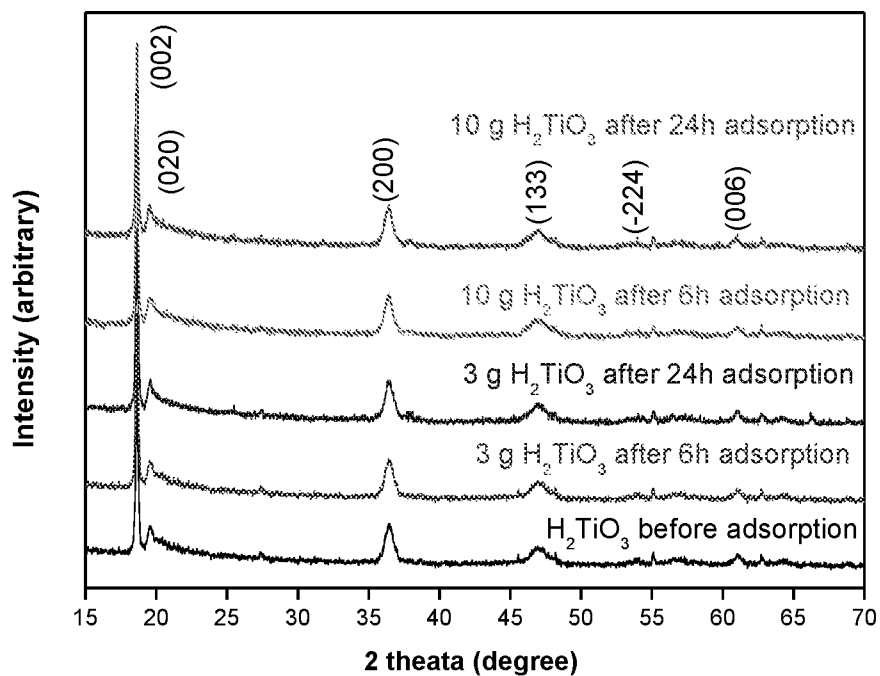


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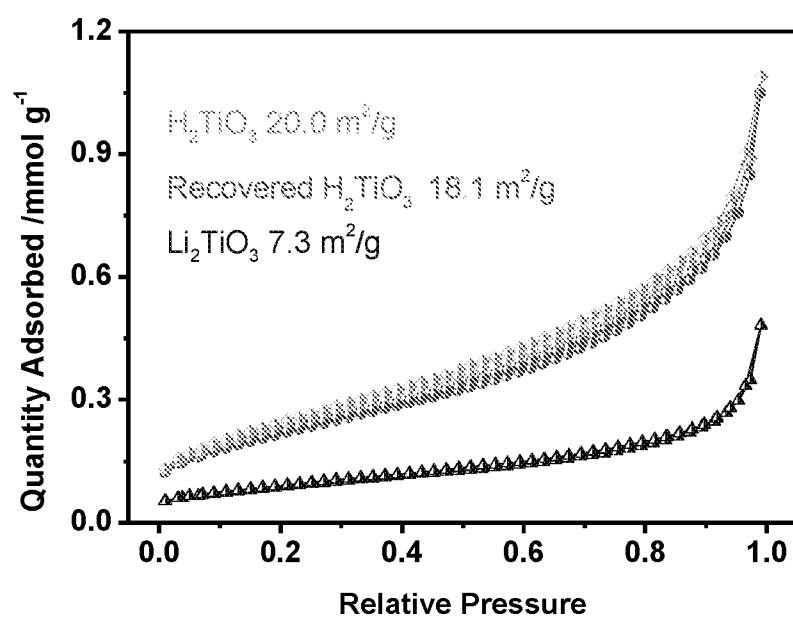


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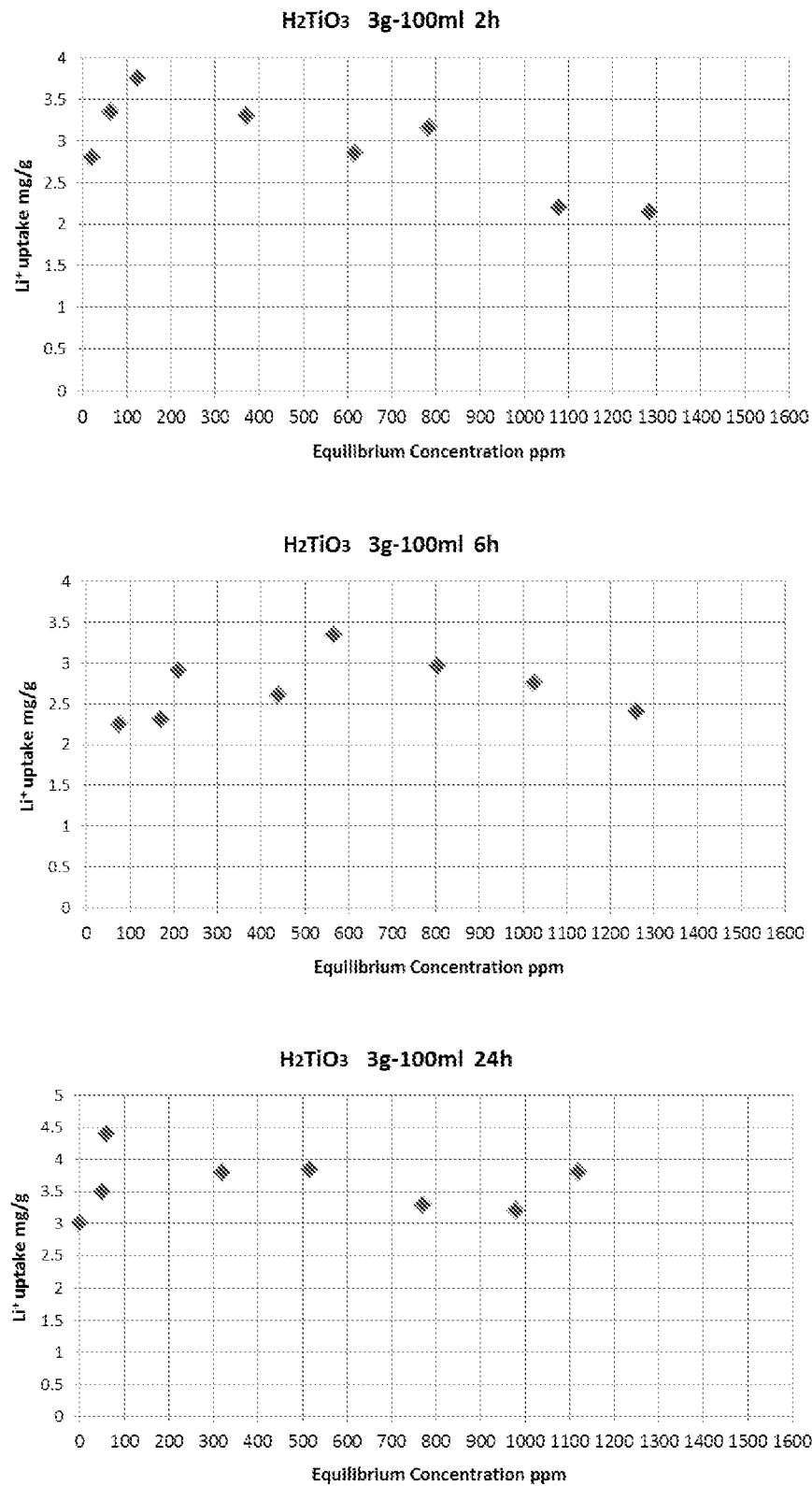


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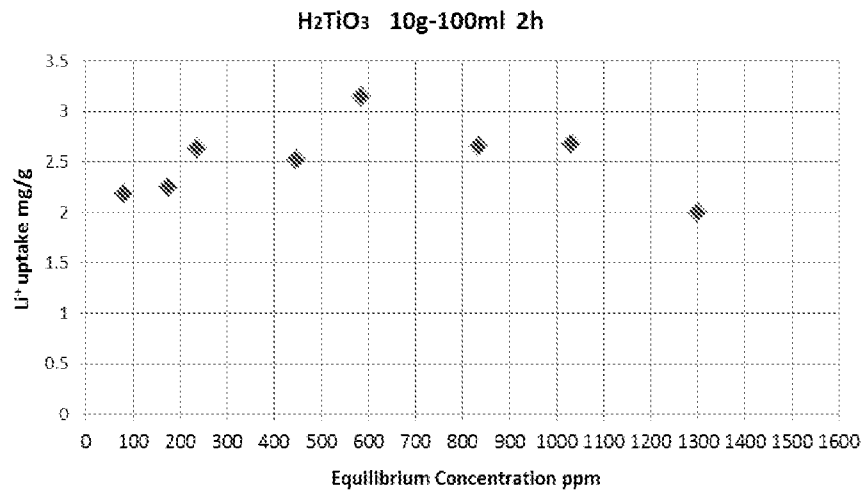
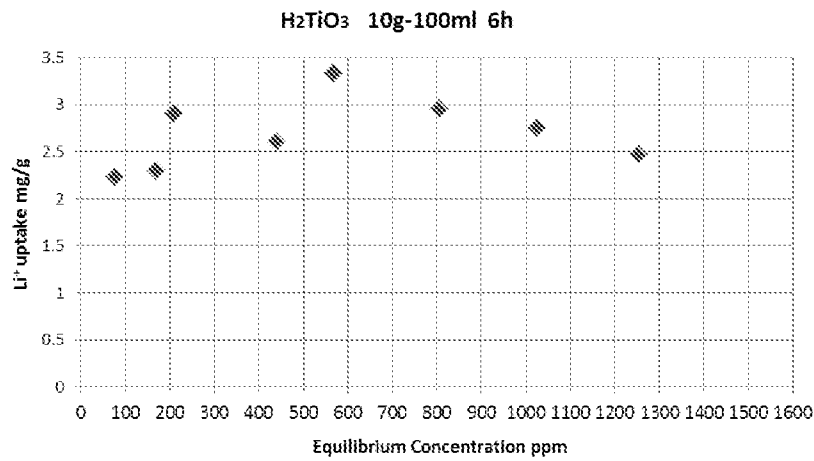
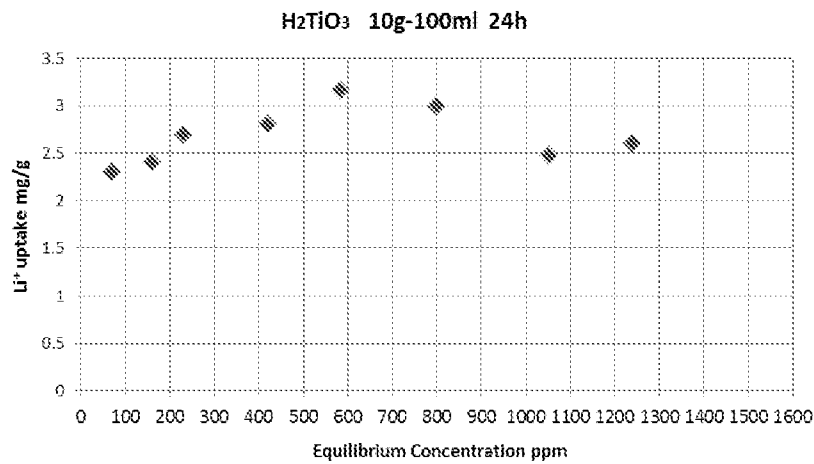


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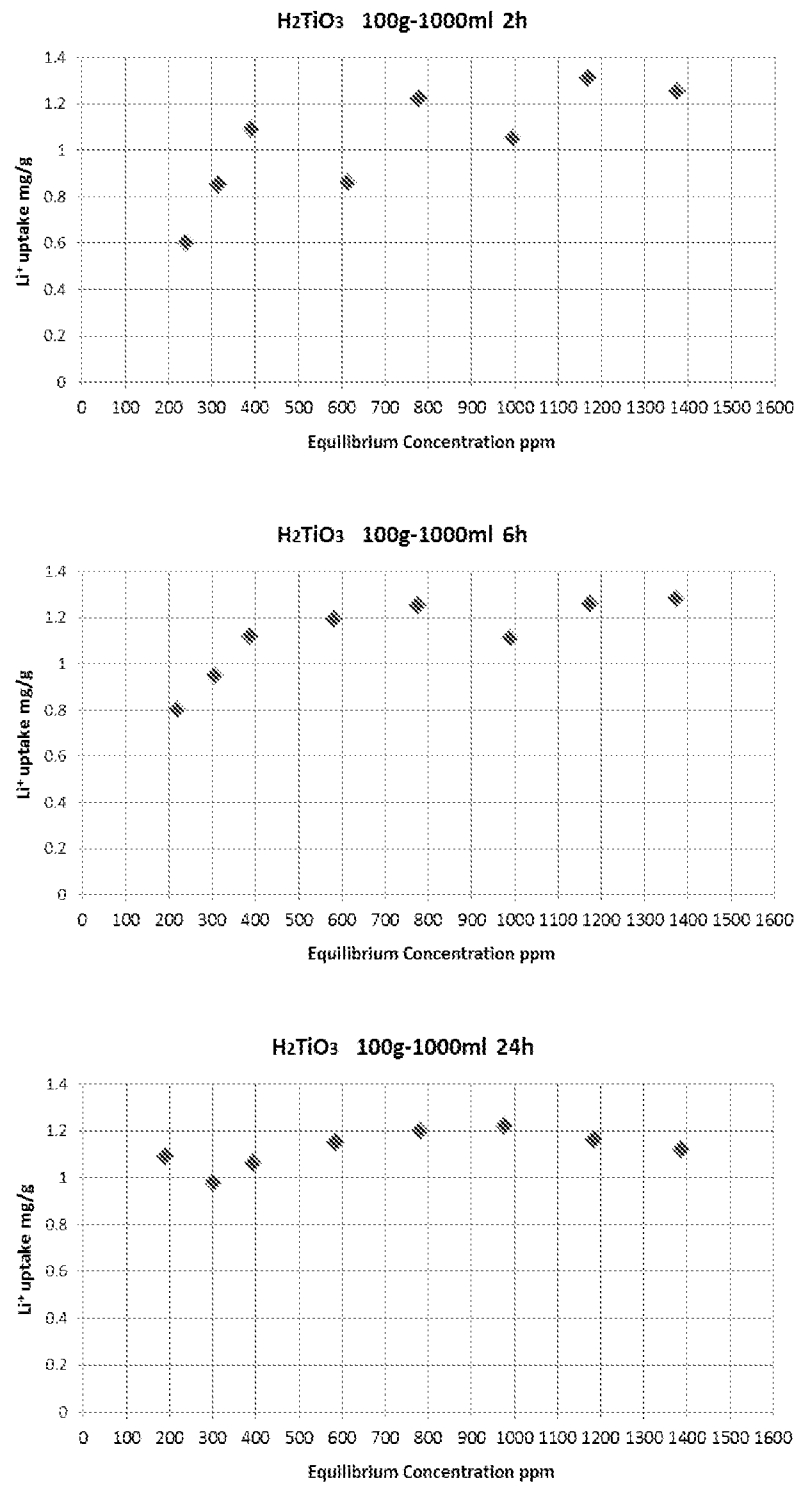


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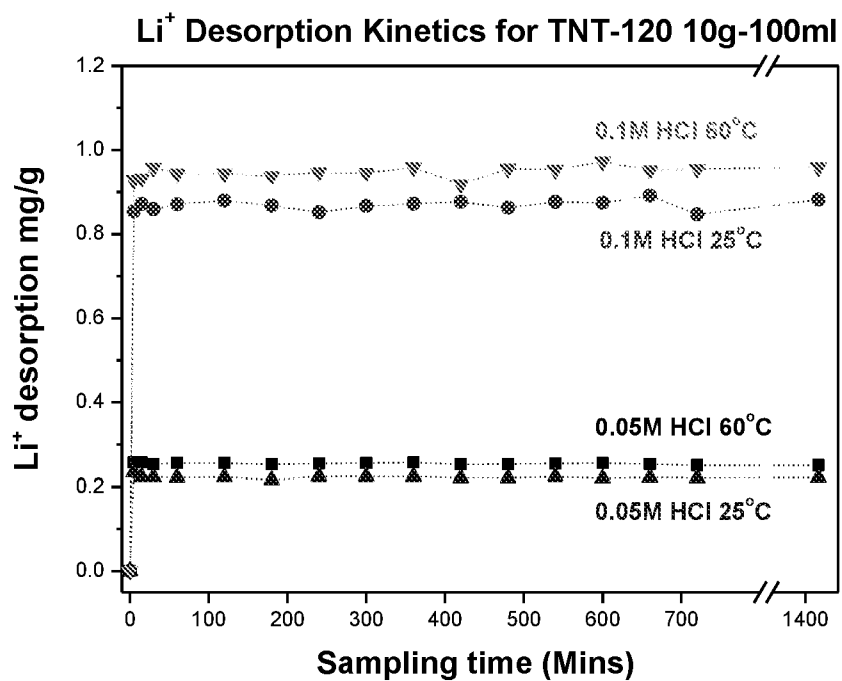


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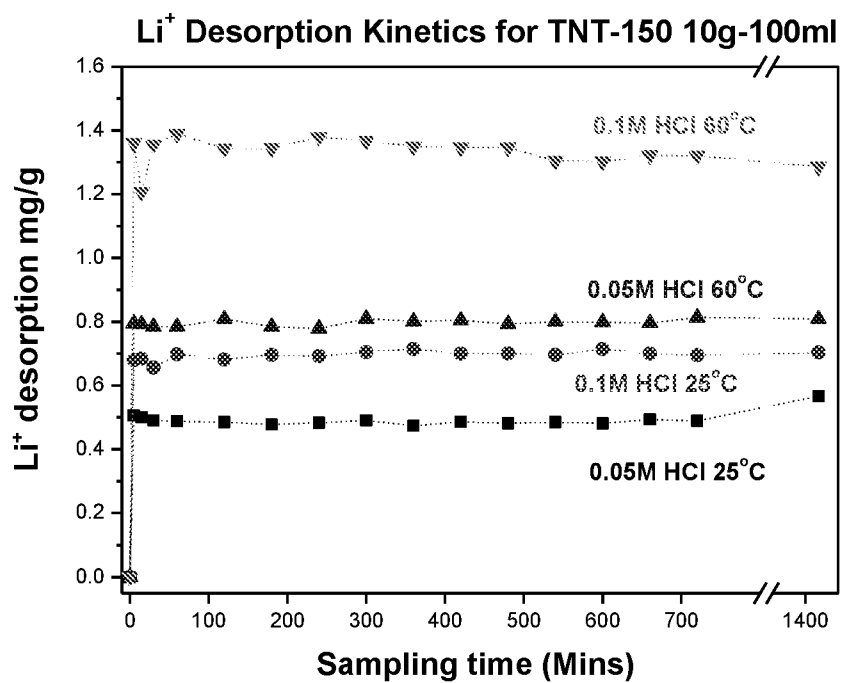


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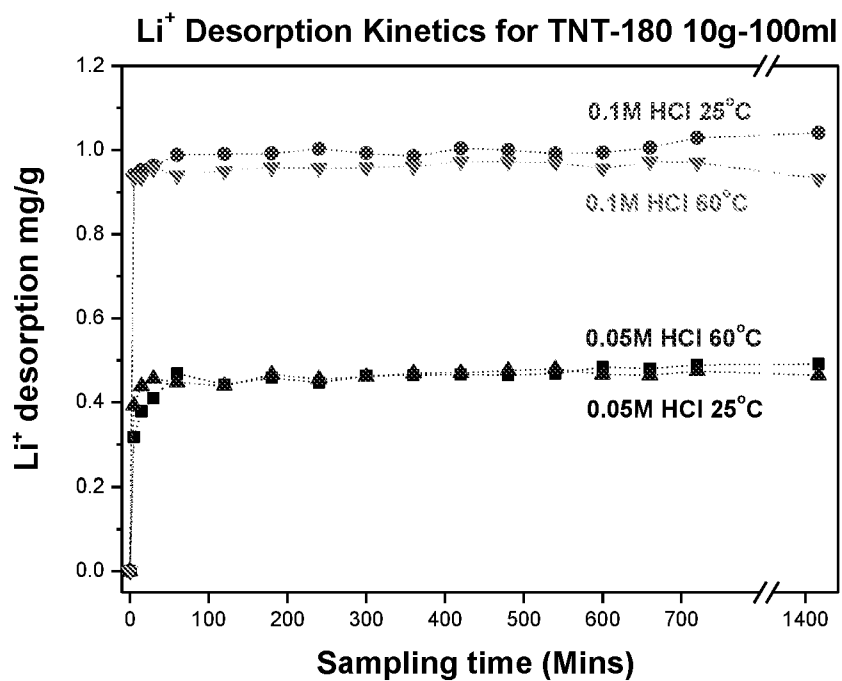


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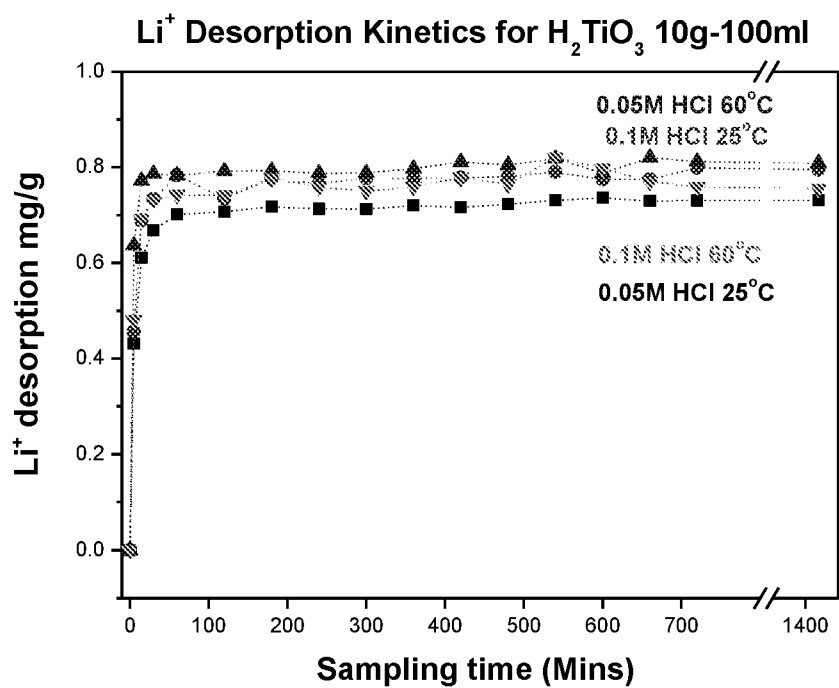


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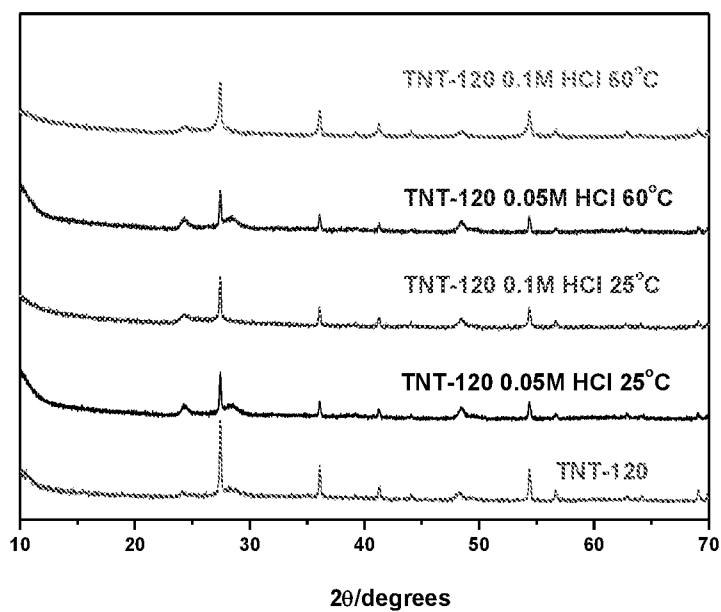


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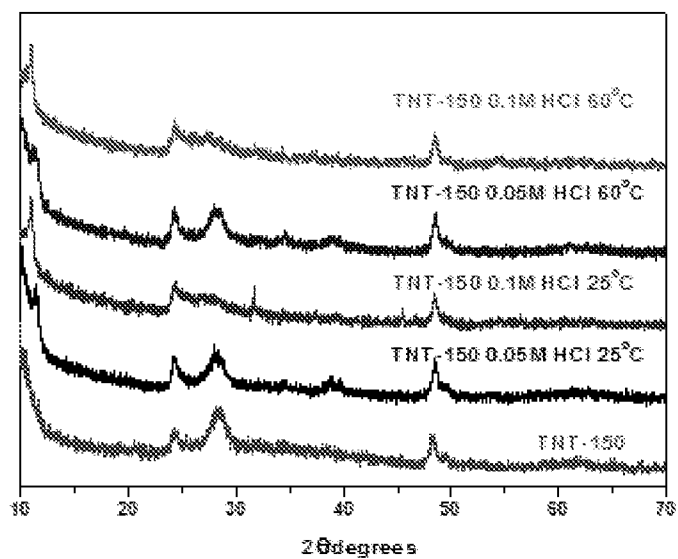


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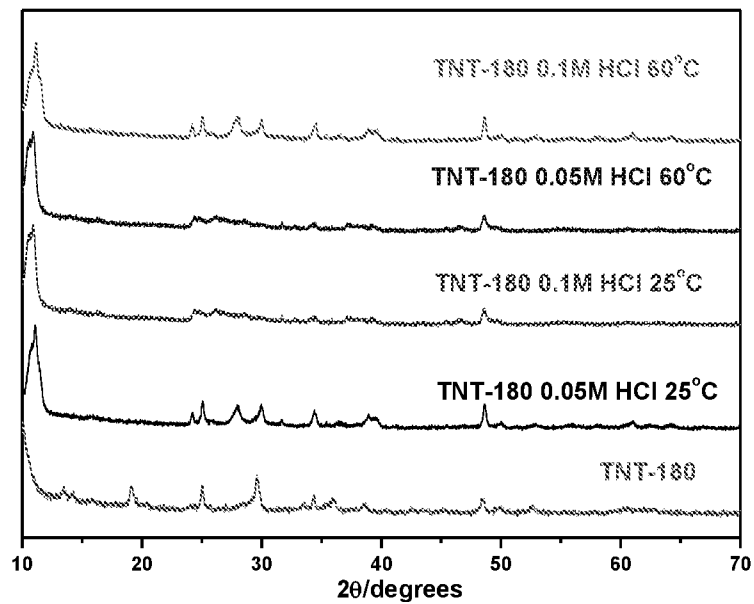


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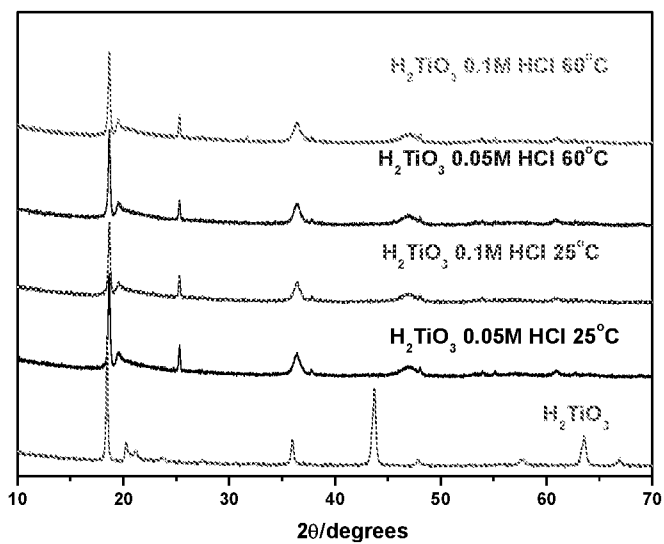
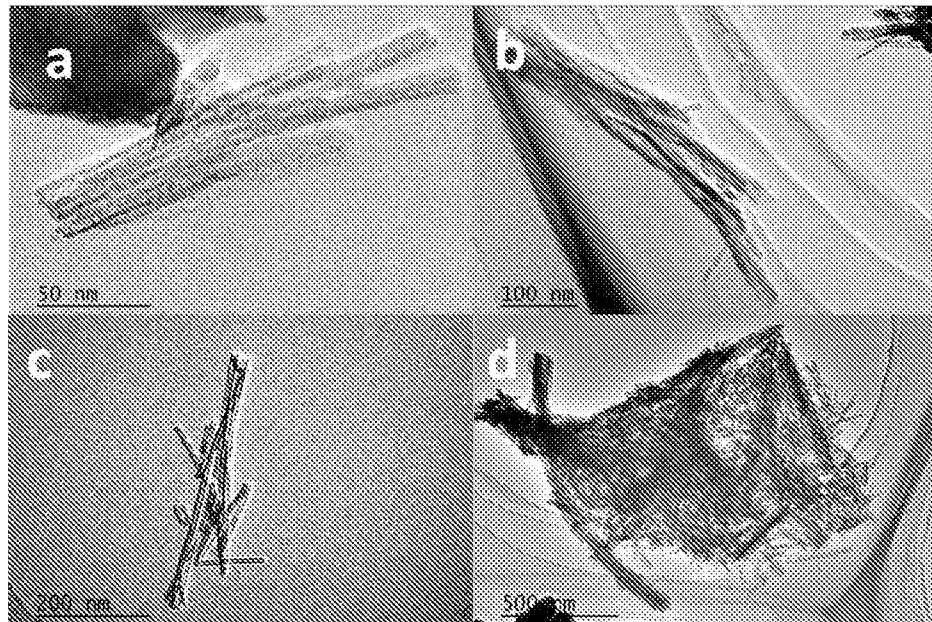
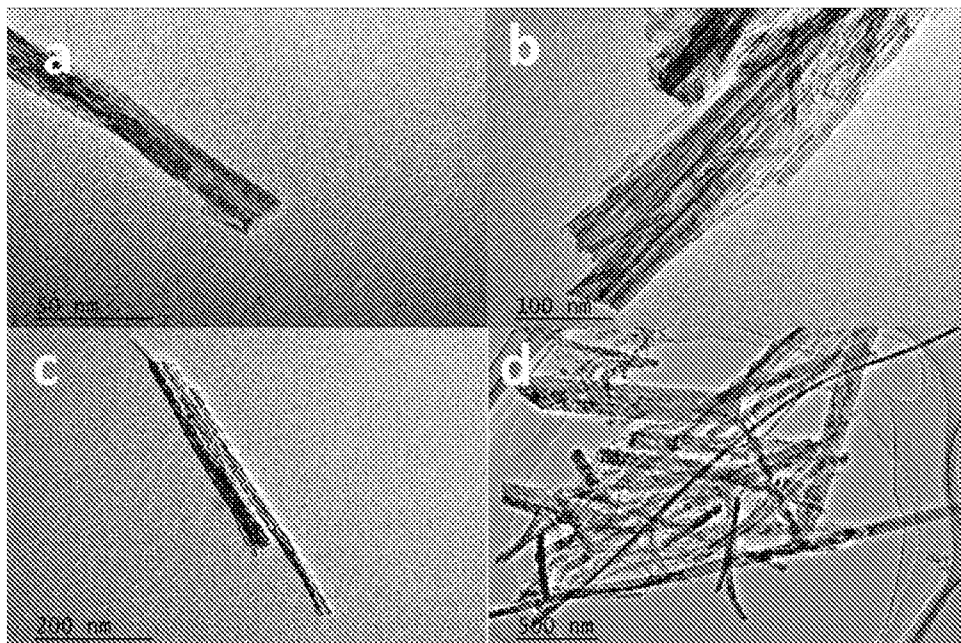


Figure 43

**Figure 44****Figure 45**

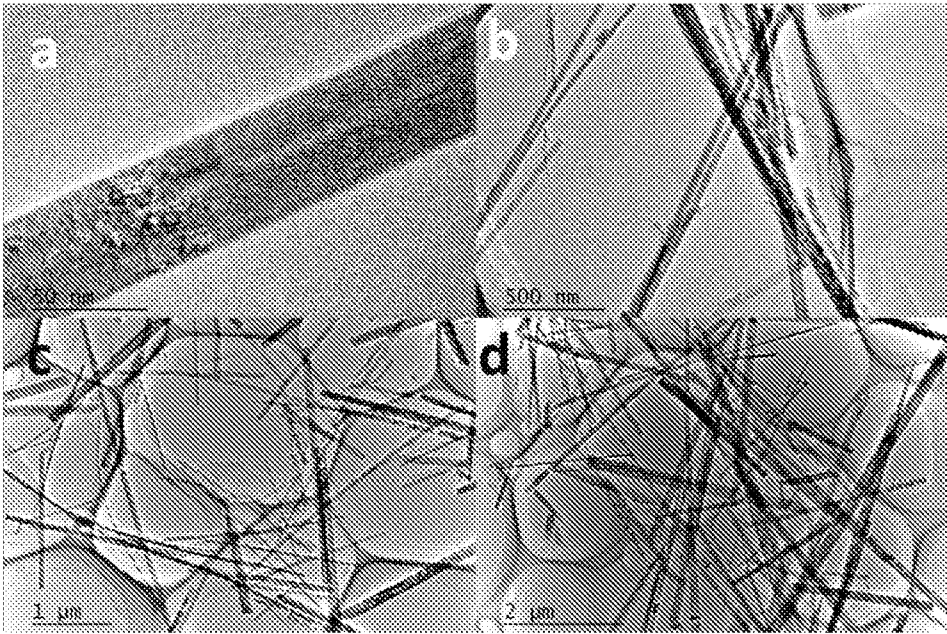


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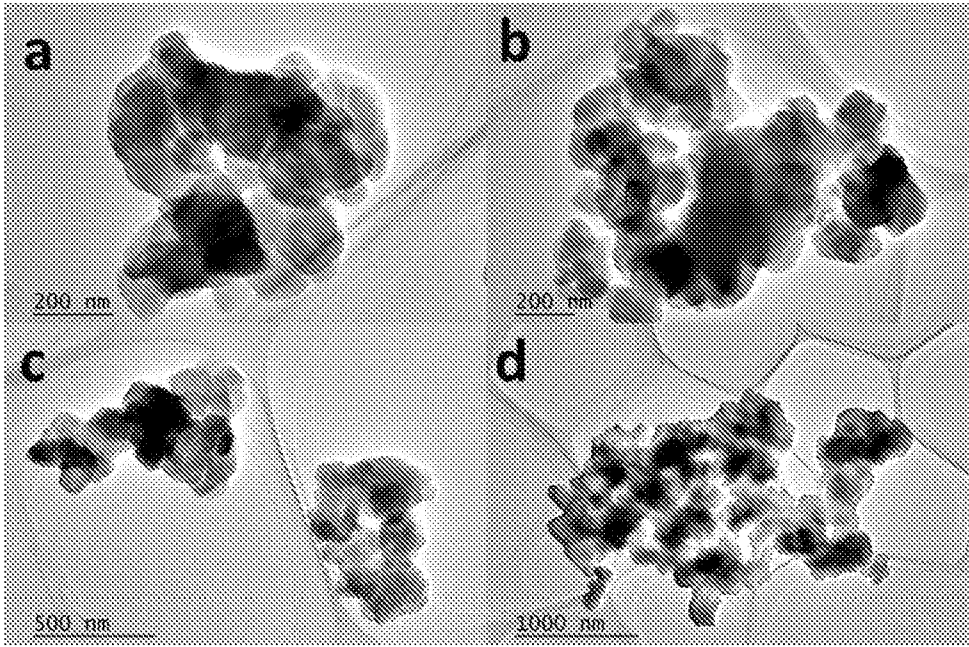


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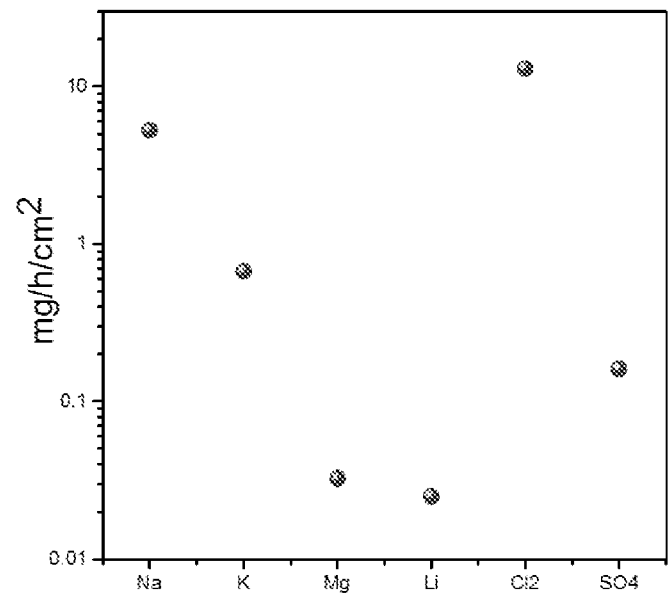


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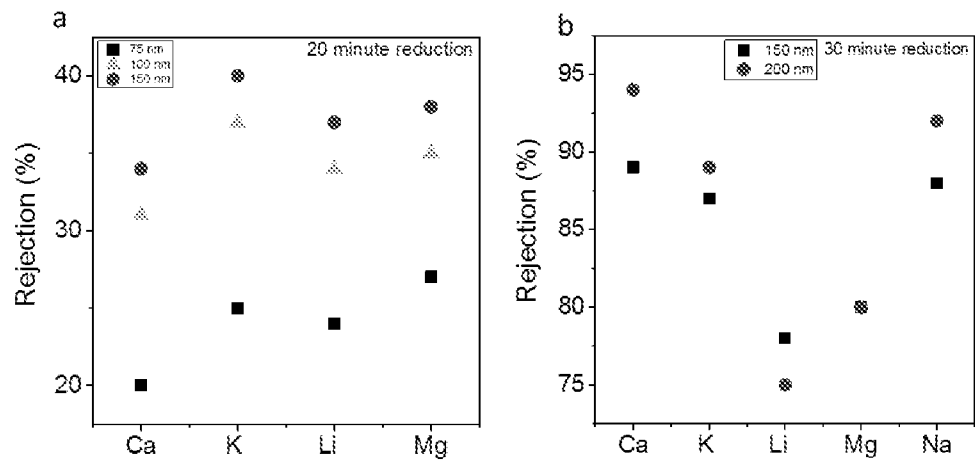


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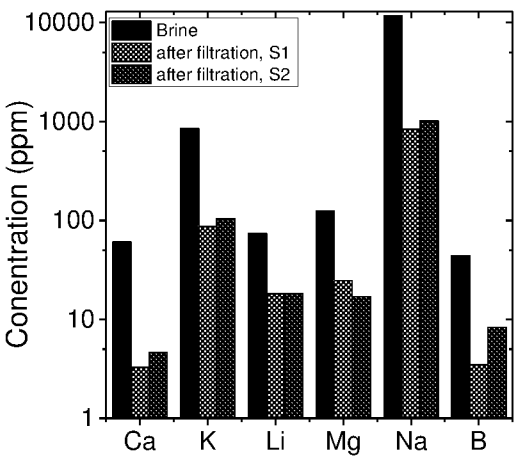


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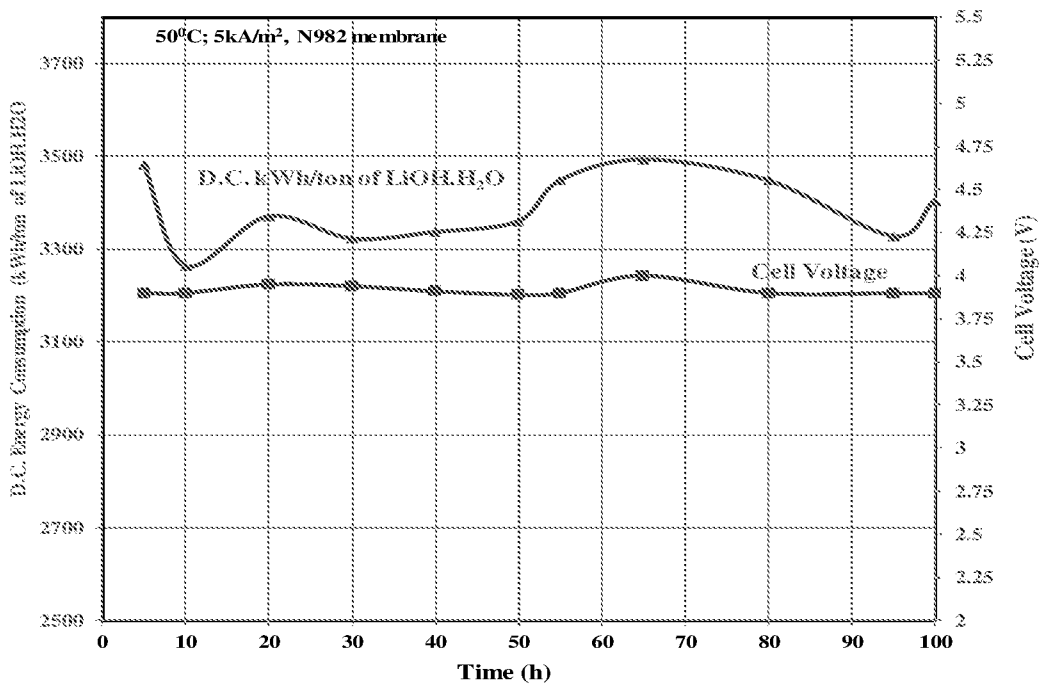


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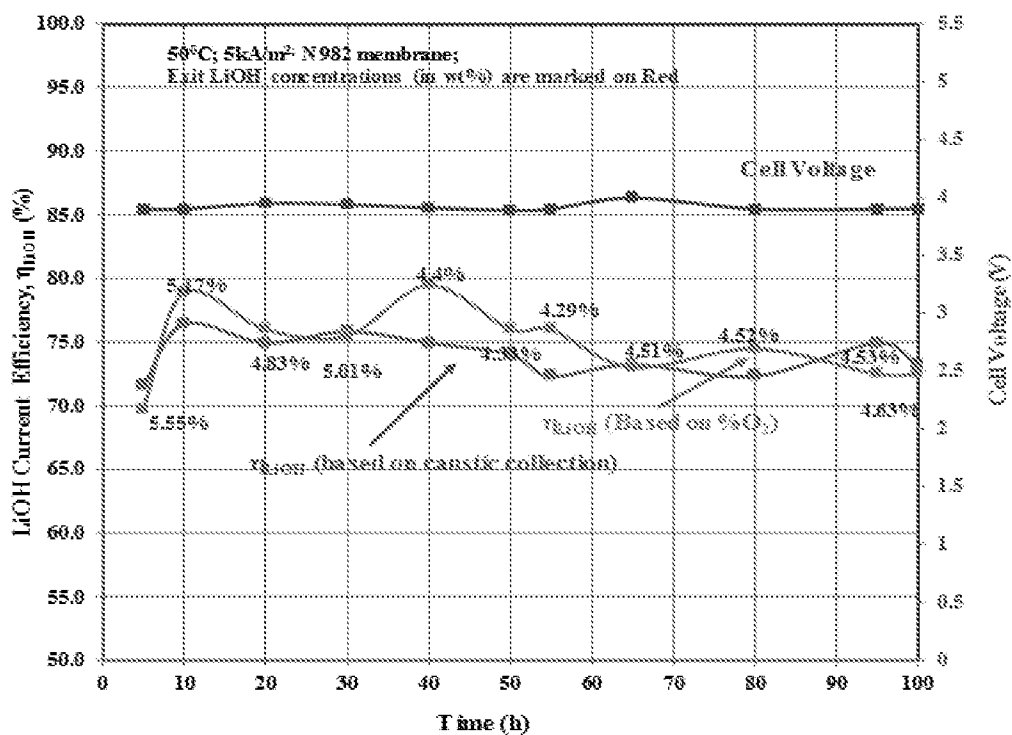


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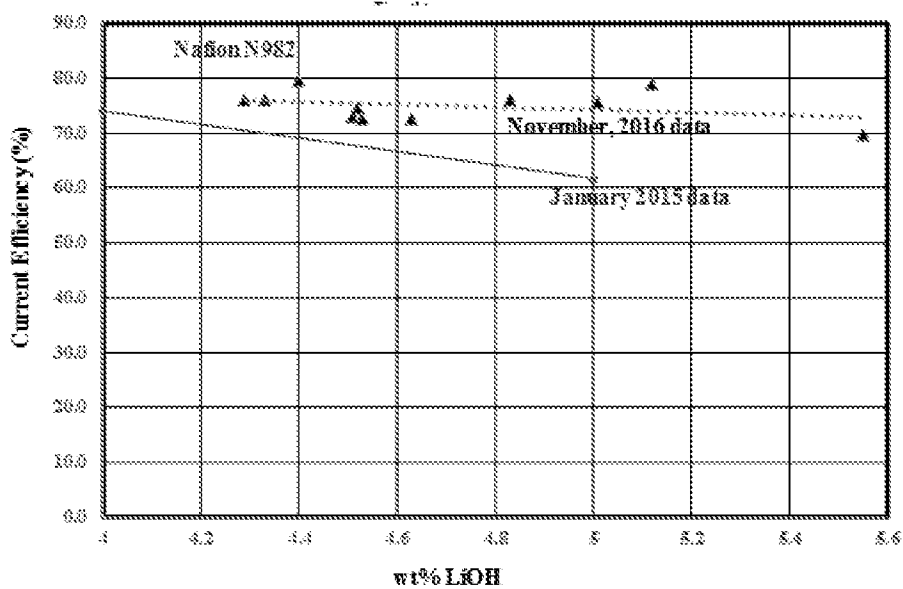


Figure 53

INTERNATIONAL SEARCH REPORT

 International application No.
PCT/AU2017/050100

A. CLASSIFICATION OF SUBJECT MATTER

C01D 15/04 (2006.01) C22B 26/12 (2006.01) C22B 3/20 (2006.01)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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)

TXPEA, TXPEB, TXPEC, TXPEE, TXPEF, TXPEH, TXPEI, TXPEP, TXPEPEA, TXPES, TXPUSE0A, TXPUSE1A, TXPUSEA, TXPUSEB, TXPW0EA, EPODOC, WPIAP: IPC & CPC: (/IC/CC) (C01D, B01D, B01J, B82, C02F, C01B31/04/LOW, C01B2204/LOW, C01D15, C22B26/12/LOW, C22B3/20/LOW) and Keywords (lithium, lithium chloride, electrolysis, lithium hydroxide, titanate, graphene and similar terms). General keyword search using the keywords ((lithium, lithium chloride, electrolysis, lithium hydroxide, titanate, graphene and similar terms)).

Google Patents, Espacenet, Google Scholar, Science Direct: Keywords (lithium chloride, electrolysis, lithium hydroxide monohydrate, lithium hydroxide, titanate, adsorb, graphene, filter and similar terms).

Applicant(s)/Inventor(s) search conducted on Espacenet, AusPat, and all internal databases provided by IP Australia.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	



Further documents are listed in the continuation of Box C



See patent family annex

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"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
"E"	earlier application or patent but published on or after the international filing date	"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
"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)	"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
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search 3 May 2017		Date of mailing of the international search report 03 May 2017	
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustalia.gov.au		Authorised officer Khalid Shamim AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. 0262832560	

INTERNATIONAL SEARCH REPORT		International application No.
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		PCT/AU2017/050100
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2015/0152523 A1 (YATENDRA SHARMA; REED INDUSTRIAL MINERALS PTY LTD.) 04 June 2015 abstract; figure 1; paragraphs [0001]-[0003], [0011]-[0024]; [0033]-[0052]; claims 1-26	1-48
A	US 6207126 B1 (BORYTA et al.) 27 March 2001 abstract; column 6, line 21-column 10, line 35; claim 1	1-48
A	US 3872220 A (SMITH, Jr.) 18 March 1975 abstract; column 1, line 57-column 8, line 5; claims 1-12	1-48

INTERNATIONAL SEARCH REPORT		International application No.	
Information on patent family members		PCT/AU2017/050100	
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.			
Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	Publication Date	Publication Number	Publication Date
US 2015/0152523 A1	04 June 2015	US 2015152523 A1	04 Jun 2015
		AU 2013201833 A1	27 Feb 2014
		AU 2013201833 B2	17 Jul 2014
		CA 2851786 A1	20 Feb 2014
		CL 2014001656 A1	10 Oct 2014
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		WO 2014026217 A1	20 Feb 2014
US 6207126 B1	27 March 2001	US 6207126 B1	27 Mar 2001
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		US 8057764 B2	15 Nov 2011
		US 2006115396 A1	01 Jun 2006
		US 2006115407 A1	01 Jun 2006
		US 3872220 A	18 March 1975
End of Annex			
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.			