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(54) **Title:**

A BINDER FOR LITHIUM ION RECHARGEABLE BATTERY CELLS

(57) **Abstract:**

An electrode for a lithium ion rechargeable battery cell is provided, the battery comprising current collectors (10, 12), a cathode layer (16), a separator and a cohesive anode mass (14), the cohesive mass comprising silicon as an active material and a polymeric binder, characterized in that the polymeric binder is a homo- polymer or copolymer of one or more monomers selected from the group consisting of acrylic acid, 3-butenoic acid, 2-methacrylic acid, 2-pentenoic acid, 2,3- dimethylacrylic acid, 3,3-dimethylacrylic acid, trans-butenedioc acid, cis- butenedioc acid and itaconic acid and optionally an alkali metal salt thereof. The silicon comprises 20 to 100% of the active material in the cohesive mass. The binder is mixed with the silicon to form the cohesive mass that adheres to the current collector and maintains said cohesive mass in electrical contact with the current collector (12).

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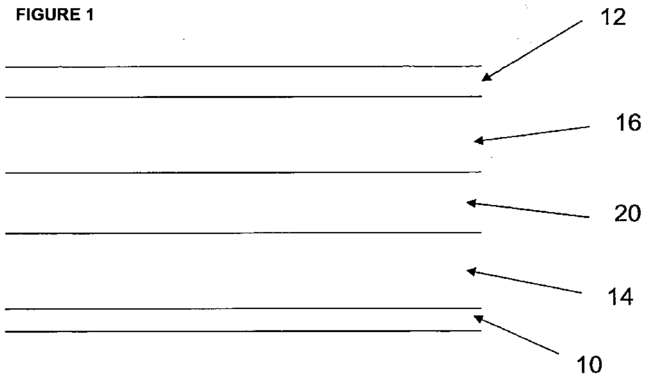
(54) **Title**: A BINDER FOR LITHIUM ION RECHARGEABLE BATTERY CELLS

FIGURE 1



(57) **Abstract**: An electrode for a lithium ion rechargeable battery cell is provided, the battery comprising current collectors (10, 12), a cathode layer (16), a separator and a cohesive anode mass (14), the cohesive mass comprising silicon as an active material and a polymeric binder, characterized in that the polymeric binder is a homo- polymer or copolymer of one or more monomers selected from the group consisting of acrylic acid, 3-butenoic acid, 2-methacrylic acid, 2-pentenoic acid, 2,3- dimethylacrylic acid, 3,3-dimethylacrylic acid, trans-butenedioc acid, cis- butenedioc acid and itaconic acid and optionally an alkali metal salt thereof. The silicon comprises 20 to 100% of the active material in the cohesive mass. The binder is mixed with the silicon to form the cohesive mass that adheres to the current collector and maintains said cohesive mass in electrical contact with the current collector (12).

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A Binder for Lithium Ion Rechargeable Battery Cells

Technical Field

The invention relates to lithium ion rechargeable battery cells and especially to a binder for use in such cells.

Background Art

Lithium-ion rechargeable battery cells currently use a carbon/graphite-based anode. The basic composition of a conventional lithium-ion rechargeable battery cell including a graphite-based anode electrode is shown in Fig. 1. A battery may include a single cell but may also include more than one cell.

The battery cell generally comprises a copper current collector 10 for the anode and an aluminium current collector 12 for the cathode, which are externally connectable to a load or to a recharging source as appropriate. It should be noted that the terms "anode" and "cathode" are used in the present specification as those terms are understood in the context of batteries placed across a load, i.e. the term "anode" denotes the negative pole and the term "cathode" the positive pole of the battery. A graphite-based composite anode layer 14 overlays the current collector 10 and a lithium containing metal oxide-based composite cathode layer 16 overlays the current collector 12. A porous plastic spacer or separator 20 is provided between the graphite-based composite anode layer 14 and a lithium containing metal oxide-based composite cathode layer 16: a liquid electrolyte material is dispersed within the porous plastic spacer or separator 20, the composite anode layer 14 and the composite cathode layer 16. In some cases, the porous plastic spacer or separator 20 may be replaced by a polymer electrolyte material and in such cases the polymer electrolyte material is present within both the composite anode layer 14 and the composite cathode layer 16.

When the battery cell is fully charged, lithium has been transported from the lithium containing metal oxide in the cathode via the electrolyte into the graphite-based anode where it is intercalated by reacting with the graphite to create a lithium carbon compound, typically LiC_6. The graphite, being the electrochemically active material in the composite anode layer, has a maximum capacity of 372 mAh/g.

It is well known that silicon can be used instead of graphite as the active anode material (see, for example, Insertion Electrode Materials for Rechargeable Lithium Batteries, M. Winter, J. O. Besenhard, M. E. Spahr, and P.Novak in Adv. Mater. 1998, 10, No. 10). It is generally believed that silicon, when used as an active anode material in a lithium-ion rechargeable cell, can provide a significantly higher capacity than the currently used graphite. Silicon, when converted to the compound $Li_{21}Si_5$ by reaction with lithium in an electrochemical cell, has a theoretical maximum capacity of 4,200 mAh/g, considerably higher than the maximum capacity for graphite. Thus, if graphite can be replaced by silicon in a lithium rechargeable battery, a substantial increase in stored energy per unit mass and per unit volume can be achieved.

In lithium-ion rechargeable battery cells using a graphite-based anode, the graphite is in the form of a fine powder whose particles are held together by a binder. Polyvinylidene fluoride (PVDF) and styrene butadiene rubber (SBR) are the most commonly used binders in graphite anodes but other binders have been suggested, for example US-5660948 discloses the following binders in a carbon anode of a lithium ion cell: ethylene-propylenediene termonomer, PVDF, ethylene-acrylic acid copolymer and ethylene vinyl acetate copolymer.

US-6399246 teaches that poly(acrylic acid) does not provide good adhesive properties in graphite anodes of lithium-ion battery cells and claims the use of a polyacrylamide binder.

US-6620547 discloses a lithium secondary cell having a carbon anode, in which lithium may be intercalated, and a cathode formed from a transition metal held by a matrix polymer. The polymer used has an affinity for the transition metal ions so that they are held on the polymer chains. The polymer may be selected from a number of materials such as polyacrylate, poly(acrylic acid), polymethylmethacrylate, poly(vinyl pyrrolidone), polyacrylonitrile, poly(vinylidene fluoride) and poly(vinyl chloride).

US5260148 discloses a lithium secondary cell having an anode formed from a lithium compound that is held together by a binder, which may be starch, carboxymethyl cellulose (CMC), diacetyl cellulose, hydroxypropyl cellulose, ethylene glycol, poly(acrylic acid), polytetrafluoroethylene and poly(vinylidene fluoride).

The most common binders used in graphite anodes of lithium ion cells (PVDF and SBR) do not bind silicon electrode material cohesively together in silicon-based anodes over successive charging cycles and it is believed that this is due to the relatively large volume changes associated with the insertion and removal of lithium ions into the silicon material during the charging and discharging stages of the cells. The volume changes are much larger than in the corresponding graphite anodes and can result in individual silicon particles not always re-establishing electrical contact with each other and with a current collector when the silicon anode shrinks due to the removal of lithium ions during discharging.

An alternative binder that has been proposed for silicon systems is sodium carboxymethylcellulose (NaCMC) Na-CMC adequately functions as a binder when used in conjunction with high purity silicon, of the type used to fabricate integrated circuit (IC) Si-wafers. However, such silicon is very expensive. When using relatively cheap, lower-grade silicon, there are minor amounts of impurities present that are not chemically compatible with the binder solution and that cause a decrease in the viscosity of the silicon / binder mixture. As a consequence, the resulting coating does not retain sufficient contact with the current collector so as to undergo anything more than a limited number of discharge / recharge cycles, before losing its capacity to hold a charge.

Journal of Applied Electrochemistry (2006) 36:1099-1104 discloses the use of an acrylic adhesive as a binder for the anode of Li-ion batteries. The anode material is a Si/C composite so has a lower volume change than electrodes where the anode is Si alone. There is no disclosure of the nature of the acrylic adhesive other than a reference to product LA132 whose composition is believed to be a mixture of acrylonitrile and butadiene in methylethyl ketone, ethyl acetate and toluene.

J Power Sources, 161 (2006), 612-616 describes a carbon anode of a lithium ion battery, which also contains NaCMC as a thickening agent and SBR as the binder. PAA (poly(acrylic acid)) is added as a surface active dispersing agent.

J Power Sources, 173 (2007), 518-521 addresses a problem of graphite electrodes for Li-ion cells when using propylene carbonate solvent/electrolyte since the propylene carbonate is intercalcated into the graphite electrode during charge/discharge, causing solvent decomposition and graphite exfoliation. The addition of PAA solves this problem.

Disclosure of the Invention

It is an object of the present invention to find a binder that can satisfactorily bind together a range of particulate silicon material, and especially particles made of the relatively cheap "lower grade" silicon, in the electrode of a rechargeable lithium ion cell over a substantial number of discharge/recharge cycle before losing its capacity to hold a charge, despite the large volume changes associated with the insertion and removal of lithium ions into the silicon material during such cycles.

Surprisingly, it has been found that poly(acrylic acid) (PAA) is a good binder for particulate silicon material in an electrode of a rechargeable lithium ion cell despite the large volume changes associated with the discharging/recharging cycles and that it can be used with both high purity (99.90% pure or above) silicon and lower purity (less than 99.90% pure) silicon.

A first aspect of the invention provides an electrode for a lithium ion rechargeable battery cell comprising:

- a current collector, and
- a cohesive mass comprising silicon as an active material and a polymeric binder, characterized in that the polymeric binder is a homo-polymer or copolymer of one or more monomers selected from the group consisting acrylic acid, 3-butenoic acid, 2-methacrylic acid, 2-pentenoic acid, 2,3-dimethylacrylic acid, 3,3-dimethylacrylic acid, trans-butenedioc acid, cis-butenedioc acid and itaconic acid, and optionally an alkali metal salt thereof, wherein the silicon comprises 20 to 100% of the active material and wherein the binder is mixed with the silicon to form a cohesive mass that adheres to the current collector and maintains said cohesive mass in electrical contact with the current collector.

The binder is suitably in the form of a homopolymer or a copolymer. Typical copolymers include alternating copolymers, block copolymers, periodic copolymers and statistical copolymers. Such polymers can be formed from different combinations of the monomer units referred to above and also from the reaction of polymer blocks formed from such monomer units.

Suitable alkali metal salts of these polymers include salts of lithium, sodium and potassium. Alkali metal salts of polyacrylic acid are preferred, especially the sodium and lithium salts thereof.

As mentioned above, although the use of poly(acrylic acid) as an alternative binder to the more commonly used PVDF and SBR binders used in graphite electrodes of lithium ion cells is known, the volume changes that occur during the charging/discharging cycles using silicon as an active material in an electrode are considerably greater than when using graphite as the active material. In addition, US-6399246 teaches that poly(acrylic acid) does not provide good adhesive (binder) properties for graphite anode material in a lithium ion cell.

The finding by the inventors that poly(acrylic acid) is able to effectively bind silicon as an active material in an electrode of a lithium ion battery is therefore both surprising and unexpected.

In contrast to NaCMC, the acrylic binders of the present invention can be used with all grades of silicon in a Li-ion electrode and enable a stable cycle life performance whilst also overcoming the potential instability of the NaCMC binder to impurity elements that can be present in lower cost grades of silicon.

Beside PAA, other polymeric acrylic acid derivatives can be used as binders, as set out in Table 1, and mixtures of such binders can also be used:

Table 1

Name	Monomer	Polymer
Acrylic acid	$CH_2:CH.COOH$	$(CH_2.CH.COOH)_n$
3-Butenoic acid (vinyl acetic acid)	$CH_2:CH.CH_2.COOH$	$(CH_2.CH.CH_2.COOH)_n$
2-Methacrylic acid	$CH_2:C(CH_3).COOH$	$(CH_2.C(CH_3).COOH)_n$
2-Pentenoic acid	$CH_3.CH_2.CH:CH.COOH$	$(CH_3.CH_2.CH.CH.COOH)_n$
2,3 Dimethylacrylic acid (tiglic acid)	$CH_3.CH:C(CH_3).COOH$	$(CH3.CH.C(CH_3).COOH)_n$
3,3 Dimethacrylic acid	$(CH_3)_2.C:CH.COOH$	$(CH_3)_2.CH.CH.COOH)_n$
Trans-butenedioic acid (fumaric acid)	$CH(COOH):CH.COOH$	$(CH(COOH).CH.COOH)_n$
Cis-butenedioic acid (maleic acid)	$CH(COOH):CH.COOH$	$(CH(COOH).CH.COOH)_n$
Itaconic acid	$CH_2:C(COOH).CH_2.COOH$	$(CH_2.C(COOH).CH_2.COOH)_n$

Co-polymers of one or more of the above polymers with each other or with other monomers containing a vinyl group e.g. vinyl acetate, can also be used, e.g. poly(acrylamide-co-acrylic acid).

A wide range of molecular weights of the poly(acrylic acid) or poly(methacrylic acid) or their derivatives may be used, for example the preferred molecular weight for PAA is greater than 50,000 (for example a molecular weight of 450,000) and also greater than 1,000,000 (for example 1,250,000).

The silicon in the electrode could be any suitable form. The silicon is suitably provided in the form of particles, fibres, sheet-like, pillar-like or ribbon-like particles (as described in WO2008/139157) or pillared particles. Fibres can be made using the techniques disclosed in WO2007/083152, WO2007/083155 and WO 2009/010758. Pillared particles are silicon particles on which pillars have been etched using the above techniques, as disclosed in WO2009/010758.

The silicon is preferably in the form of particles, fibres or pillared particles or a mixture thereof. Silicon particles typically have a diameter in the range 3 to 15μm, preferably 4.5μm. The silicon fibres typically have a diameter in the range 80 to 500nm and a length in the range 20 to 300μm. Pillared particles typically have a diameter in the range 15 to 25μm and a pillar height in the range 1 to 4μm. In addition to silicon as an active material, the cohesive mass may also include within the mix other active materials such as graphite or hard carbon and/or conductive materials, such as carbon black, acetylene black or ketjen black.

The silicon is preferably the cheaper silicon that gives rise to problems with a NaCMC binder discussed above; such silicon will generally have a purity of less than 99.800%, although the surface area of the silicon also seems to have an effect on the level of the impurities that give rise to electrode deterioration. However, the purity should generally be greater than 95.00% by mass in order to ensure that there is sufficient silicon to intercalate the lithium and preferably the purity is greater than 98%. The silicon may include a wide range of impurities, principally iron, aluminium, calcium, titanium, phosphorous, boron and/or carbon present in an amount of up to about 0.2% each.

The silicon granules used to prepare the silicon fibres and pillared particles that are used in the fabrication of the electrodes of the present invention may be crystalline for example mono- or poly-crystalline. The polycrystalline particle may comprise any number of crystals for example two or more.

It will be appreciated that the electrodes of the first aspect of the invention comprise, in addition to a current collector, a cohesive mass, which comprises an active material, a binder and optionally a conductive material. By the term “active material” it should understood to mean (in the context of lithium ion batteries) a material, which is able to incorporate lithium into and release lithium from its structure during the charging and discharging cycles of the battery respectively. The silicon preferably comprises 20 to 100% of the active material in the cohesive mass. Other active materials may be added. Suitable active materials include graphite and hard carbon. In a first embodiment of the electrode of the first aspect of the invention the active material comprises 20 to 100% silicon and from 0 to 80% of an active carbon selected from the graphite and/or hard carbon.

The cohesive mass suitably comprises 50 to 95% active material, preferably 60 to 90% and especially 70 to 80%.

The binder of Table 1 can be used in a mixture with other binders and should form at least 10% by weight, preferably at least 25%, and optionally the binder of Table 1 comprises at least 90% by weight of the total binder content in the electrode. In particular, poly(acylic acid) (PAA) / carboxymethyl cellulose (CMC) combinations and PAA and polyvinyldifluoride (PVDF) combinations should be mentioned.

The cohesive mass suitably comprises 5 to 20% by weight binder, preferably 8 to 15% by weight and especially 8 to 12% by weight binder. Binder contents of 12% are most preferred.

As indicated above, the cohesive mass may optionally include a conductive material. Examples of suitable conductive materials include carbon black, acetylene black, ketjen black, channel black; conductive fibres such as carbon fibres (including carbon nanotubes). The cohesive mass suitably comprises 10 to 30% conductive carbon, preferably 8 to 20% and especially 12 to 14%.

Description of the Drawing

Fig. 1 is a schematic representation of a lithium ion cell;
Figures 2 – 7 are graphs showing the results of Examples 2-7

Specific Description of preferred embodiments

Example 1- Preparation of Electrodes and Testing of Binders

A series of binders were tested by making up anodes using silicon powder as the active material, the binder set out in Table 2 and a conductive carbon black (Super P ® carbon black obtained from TIMCAL, Strada Industriale, CH-6743 Bodio, Switzerland, or Denka Black obtained from Denka (Denki Kagaku Kogyo Kabushiki Kaisha, Tokyo) or a mixture thereof) in a ratio of silicon active material : binder :carbon black of 80 : 8 : 12 (wt%) or 76:12:12 (wt%). The polymer solutions are pre-made by dissolving the polymer solid material into the appropriate solvent either water or an organic solvent, as set out in Table 2. Specific composite mixes commence with dispersion of the relevant wt.% of the Si active material into a 10-15wt% bead-milled solution of the carbon black (Super P carbon or Denka Black) by shear stirring for 12 hours. The relevant wt% of polymer solution is then added to this and the resulting composite is subjected to Dual Asymmetric Centrifugation dispersion for 20 minutes.

Alternatively the carbon black may be dispersed into the polymer solution by shear stirring. The silicon material is then added to polymer/carbon mix with a further shear stirring step.

The resultant mix is deposited as a thin 'wet' film onto a copper foil substrate using a draw down blade. The deposited film is left to dry (preferably on a hot-plate at 50 to 70°C) such that all the solvent (water or organics) is removed to leave the dried composite electrode adhered to the copper foil substrate, which acts as a current collector in the battery cell.

The silicon active material used for testing the binder compositions was one of: (a) silicon powder "J230" from Elkem in Norway which has a mean particle diameter of 4.5µm, or (b) pillared particles (referred to in Table 2 as "PP"), which are made according to the procedure disclosed in WO2009/010758, or (c) fibres (referred to in Table 2 as "F+"), which are the pillars of the pillared particles once they have been separated from the core of the pillared particles as disclosed in WO 2009/010758.

Chemical analysis of Jetmilled Silgrain® HQ (used as the starting material in the preparation of pillared particles and fibres described in WO2009/010758 and also the brand that J230 material belongs to) from a batch analysis reported as below

Analysis:	Si wt%	Fe wt%	Al wt%	Ca wt%	Ti wt%
Max	99,7	0,05	0,12	0,02	0,003
Min	99,6	0,03	0,09	0,01	0,001
Typical	99,6	0,04	0,11	0,02	0,0021

The composite electrodes containing the silicon, polymer binder material and carbon, were incorporated into a cell with a lithium metal counter electrode, a microporous separator and an electrolyte in the form of 1.2 mol dm^{-3} lithium hexafluorophosphate in an ethylene carbonate / ethyl methyl carbonate mixture. Discrete samples of the dried composite electrode (containing the silicon, polymer and carbon) of an approximate area of 15 cm^2 were assembled in a dry environment with a similar sized area of metallic lithium between which was placed a microporous separator. The cell structure was soaked in the electrolyte solution prior to heat sealing in an aluminium laminate packaging material such that composite electrode and metallic lithium counter electrode could be connected externally via two terminals. The cells were tested for first cycle losses (FCL) by measuring the difference between the charge and discharge capacity (a product of the current and time) for the first charge/discharge cycle of the cell.

The number of charge/discharge/ cycles that could be performed reversibly before the capacity of the cell had reached less than 50% of the initial charge capacity was recorded on a computer controlled battery test station. The computer measures the charge and discharge capacity for each cycle and determines the cycle number at which the discharge capacity is less than 50% of the maximum discharge capacity. A summary of the results are set out in Table 2:

Table 2

Polymer	Solvent	Forms of Active Material Tested	Best FCL %	No. of cycles vs Li
(1) CMC	Water	J230, PP, F+	9.3	11
(2) PVP	Water	J230	96.9	1
(3) PVDF	NMP	J230	12.7	7
(4) PMMA	NMP	J230	89.8	2
(5) Ethyl Cellulose	NMP	J230	98.6	1
(6) PAA	NMP	J230, PP	8.2	21
(7) PAN	DMF	J230	15.7	11
(8) PAA	Water	J230, PP, F+	9.8	17
(9) PP	Water	J230	25.9	4
(10) SBR emulsion	-	J230	30.6	3
(11) SAN	MEK	J230	94.5	2
(12) PAM	Water	J230	12.5	7
(13) PVDC	NMP	J230	-	-
(14) PAA	Methanol	PP	32.1	14
(15) PVC	THF	J230	-	-
(16) PAA /CMC (2 : 1)	Water	J230, PP, F+	11.4	10

The abbreviations used in Table 2 are set out in Table 3::

Table 3 - Abbreviations

CMC	Carboxymethyl Cellulose
PVP	Polyvinylpyrrolidone
PVDF	Polyvinyldifluoride
PMMA	Polymethylmethacrylate
PAA	Polyacrylic Acid
PAN	Polyacrylonitrile
PP	Polypyrrole
SBR	Styrene butadiene rubber
SAN	Styrene-acrylonitrile
PAM	Polyacrylamide
PVDC	Polyvinyldichloride
PVC	Polyvinylchloride
NMP	n-Methylpyrrolidone
DMF	Dimethylformamide
MEK	Methyl Ethyl Ketone
THF	Tetrahydrofuran

As can be seen from Table 2, PAA binders provided a first cycle loss (FCL) and a lifetime (in terms of the number of cycles) exceeding other binders, especially in NMP solvent.

All lithium ion cells have some first cycle loss. An FCL value > 20 % indicates that the binder is not maintaining electrical contact between the silicon particles and the copper current collector, as the silicon particles expand and contract.

Some tests were performed using an active material (Si) : Binder : Carbon ratio (in wt %) of 74 : 13 : 13, with polymer binders NaCMC (using a water based solvent) and PAA (using both water and organic solvents) and such composite anodes produced first cycle losses in the region of 8 – 9% FCL.

Example 2 – Measuring First Cycle Loss

Using the same cell structure and method of manufacture as in Example 1, cells with various binders as per Table 2 were formed and tested for FCL. The results of the FCL tests for the various binders are shown in the bar chart of Figure 2. It should be noted that Table 2 includes a wider range of experiments including the different composition ratios such as 74:13:13 whereas Figure 2 is based on a standard formulation of 80:8:12.

Example 3

Using the same cell structure and method of manufacture as in Example 1, cells with various binders were formed as per Table 2 and tested to find the effect of the anode binder on the cycling capacity and the results are shown in the bar chart of Figure 3. Figure 3 shows the total delithiation capacity for silicon powder composite electrodes with a lithium metal counter electrode. Delithiation capacity is the amount of lithium capacity in mA hr from the test sample cells associated with the electrochemical step equivalent to the discharge in a real Li-ion cell (i.e. where lithium is removed from the silicon material) The total delithiation capacity is the cumulative amount of capacity from the all the cycles up to the point where the test cell was deemed to have failed.

Lithium metal electrodes have a limited cycle life, because of the porous and non-uniform deposits that form when lithium is plated back on to the anode during recharging. Typically, the total amount of capacity that can be passed with the standard cell construction is 500 – 600 mA hr, before the lithium electrode fails. Therefore, if the capacity is > 500 mA hr, the cell has failed because of the lithium metal counter electrode. However, if the capacity is < 500 mA hr, the cell has failed because of the silicon powder composite electrode. Therefore, most of the binders do not allow the electrode to cycle well.

Example 4

Using the same cell structure and method of manufacture as in Example 1, cells with various binders were formed using the solvents as per Table 2 and tested to find the effect of binder on the cycling capacity of the cell.

The results are shown in Figure 4, which shows the delithiation capacity of the Silgrain® HQ J230 silicon powdercomposite electrodes, using four different types of binder; PVDF, SBR, NaCMC and PAA. The lithiation capacity on the first cycle was limited to 1200 mA hr g^{-1}, based on the weight of silicon powder in the electrode. Lithiation on subsequent cycles was limited to a charge and / or voltage limit.

As explained above, the cycling of these cells is ultimately limited by the lithium metal counter electrode. However, it is evident that the cells with both PVDF and SBR lose capacity much earlier – before the lithium metal counter electrode is compromised.

Example 5

Various cells were made using the following methodology:

An active mass was applied to a copper substrate to form an anode and the assembly was dried, as described in Example 1. The cathode materials used in the cells were commercially supplied standard cathode materials and were used together with an aluminium current collector. Anodes and cathodes of the required size were cut out and then re-dried overnight at 120°C, under dynamic vacuum. Tags were ultrasonically welded to the anode and cathode, to allow the cells to be sealed inside an aluminium laminate bag and the electrodes were then assembled with one layer of Tonen™ porous polyethylene separator between them, wound into a roll and placed in the laminate bags. The cell windings were sealed inside the bags, with one edge left unsealed to allow for electrolyte filling.

The cells were filled with the required weight of electrolyte, under partial vacuum. The electrolyte was 1 M $LiPF_6$ in 3:7 EC (ethylene carbonate):EMC (ethyl methyl carbonate),. The electrolyte was allowed to soak into the electrodes for one hour and the final edge of the bag was then vacuum sealed.

The cells were connected to an Arbin™ battery cycling rig, and tested on continuous charge and discharge cycles. The test protocol used a capacity limit and an upper voltage limit on charge, and a lower voltage limit on discharge. The cells were charged up to a capacity of 1200mAhr/g.

A series of binders were tested by making up anodes using the above methodology; the active anode mass was J230 silicon powder (sold as one of the Silgrain HQ products from Elkem, Norway), the binders set out in Table 4 and a conductive carbon black (Super P ® carbon black) in a ratio of silicon active material (A) : binder (B) : Super P ® carbon (C) set out in Table 4.. Table 4 also sets out the cathode used in the various tests, where "MMO" stands for a mixed metal oxide (specifically $Li_{1+x}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ where $0<x<1$, preferably $0.05<x<0.1$) cathode and "LCO" stands for a lithium cobalt oxide ($LiCoO_2$) cathode, both of which are well-known and are commercially available.

Table 4

I. D.	Binder	Composition A : B : C	Cathode
1	PAA	76 : 12 : 12	MMO
2	NaCMC	80 : 8 : 12	LCO
3	PVDF	65 : 15 : 20	MMO
4	PVA	80 : 8 : 12	LCO
5	SBR	70 : 16 : 14	LCO
6	PAM-co-AA	76 : 12 : 12	LCO
7	PBMA	76 : 12 : 12	LCO
8	PMA-OD	76 : 12 : 12	LCO

The abbreviations in Table 4 are set out in Table 5

Table 5

PAA	Poly(acrylic acid)
NaCMC	Sodium carboxymethyl cellulose
PVDF	Polyvinyldifluoride
PVA	Polyvinyl alcohol
SBR	Styrene Butadiene Rubber
PAM-co-AA	Polyacrylamide acrylic acid copolymer
PBMA	Poly(butyl methacrylate)
PMA-OD	poly(maleic anhydride-alt-1-octadecene)

Figure 5 shows the effect of different binders on the discharge capacity during constant charging/discharging cycling. As can be seen, PAA binders provided substantially better maintenance of discharge capacity compared to other cells.

Example 6 – Silicon Fibres

Binders were tested by making up anodes using the methodology of Example 5 except that silicon fibres prepared using the methods set out in WO 2007/083152 or WO 2007/083155 were used instead of silicon powder. Such fibres typically have a diameter in the range 80 to 500nm and a length in the range 20 to 300μm. The binders and other variables in the cells are set out in Table 6.

Table 6

I. D.	Binder	Composition A : B : C	Cathode
1	PAA	80 : 8 : 12	LCO
2	PAA (NMP)	80 : 8 : 12	LCO
3	NaCMC	80 : 8 : 12	LCO
4	PVDF-g-AA	80 : 8 : 12	LCO
5	PVDF	74 : 14 : 12	MMO
6	MHPC	80 : 8 : 12	LCO
7	PE	74 : 14 : 12	MMO
8	PVPS	80 : 8 : 12	LCO
9	PE-MA-GM	80 : 8 : 12	LCO
10	PMA-O	80 : 8 : 12	LCO

The abbreviations in Table 6 are set out in Table 7

Table 7

PAA	Poly(acrylic acid)
PAA (NMP)	Poly(acrylic acid) using NMP solvent
NaCMC	Sodium carboxymethyl cellulose
PVDF-g-AA	Polyvinyldifluoride graft polymer with acrylic acid
PVDF	Polyvinyldifluoride
MHPC	Methylhydroxypropylcellulose
PE	Polyethylene
PVPS	Polyvinylpyrrolidone-co-styrene
PE-MA-GM	Poly-ethylene-maleic anhydride-glycidyl methacrylate
PMA-OD	Poly(maleic-anhydride-alt-1-ocatdecene)

Figure 6 shows the effect of different binders on the discharge capacity during constant charging/discharging cycling. As can be seen, PAA binders provided substantially better maintenance of discharge capacity compared to the binders used in the other cells.

Example 7 – Silicon Powder Particles

Binders were tested by making up anodes using the methodology of Example 5 except that the silicon is in the form of pillared particles prepared according to the methods set out in WO 2009/010758, (which have a diameter in the range 15 to 25μm and a pillar height in the range 1 to 4μm) instead of silicon powder. The binders and other variables in the cells are set out in Table 8.

Table 8

I. D.	Binder	Composition A : B : C	Cathode
1	PAA	80 : 8 : 12	LCO
2	NaCMC	80 : 8 : 12	LCO
3	PVDF-g-AA	76 : 12 : 12	MMO
4	PVDF	80 : 8 : 12	MMO
5	Polyimide	80 : 8 : 12	MMO

Figure 7 shows the effect of different binders on the discharge capacity during constant charging/discharging cycling. As can be seen, PAA binders provided substantially better maintenance of discharge capacity compared to the binders used in the other cells.

Claims

1. An electrode for a lithium ion rechargeable battery cell comprising:
   - a current collector, and
   - an cohesive mass comprising silicon as an active material and a polymeric binder, characterized in that the polymeric binder is a homo-polymer or copolymer of one or more monomers selected from the group consisting of acrylic acid, 3-butenoic acid, 2-methacrylic acid, 2-pentenoic acid, 2,3-dimethylacrylic acid, 3,3-dimethylacrylic acid, trans-butenedioc acid, cis-butenedioc acid and itaconic acid and optionally an alkali metal salt thereof, wherein the silicon comprises 20 to 100% of the active material and wherein the binder is mixed with the silicon to form a cohesive mass that adheres to the current collector and maintains said cohesive mass in electrical contact with the current collector.

2. An electrode according to claim 1 wherein the
   - silicon material forms at least 50wt% of the active material in the electrode; and the polymeric binder is taken from one of the following

Name	Monomer	Polymer
Acrylic acid	$CH_2:CH.COOH$	$(CH_2.CH.COOH)_n$
3-Butenoic acid (vinyl acetic acid)	$CH_2:CH.CH_2.COOH$	$(CH_2.CH.CH_2.COOH)_n$
2-Methacrylic acid	$CH_2:C(CH_3).COOH$	$(CH_2.C(CH_3).COOH)_n$
2-Pentenoic acid	$CH_3.CH_2.CH:CH.COOH$	$(CH_3.CH_2.CH.CH.COOH)_n$
2,3 Dimethylacrylic acid (tiglic acid)	$CH_3.CH:C(CH_3).COOH$	$(CH3.CH.C(CH_3).COOH)_n$
3,3 Dimethacrylic acid	$(CH_3)_2.C:CH.COOH$	$(CH_3)_2.CH.CH.COOH)_n$
Trans-butenedioic acid (fumaric acid)	$CH(COOH):CH.COOH$	$(CH(COOH).CH.COOH)_n$
Cis-butenedioic acid (maleic acid)	$CH(COOH):CH.COOH$	$(CH(COOH).CH.COOH)_n$
Itaconic acid	$CH_2:C(COOH).CH_2.COOH$	$(CH_2.C(COOH).CH_2.COOH)_n$

and co-polymers thereof in which the above polymers form the majority of the monomer units, the binder being mixed with the silicon material (e.g. particles, fibres, structoids or pillared particles) to form a cohesive mass that adheres to the current collector and maintains the mass in electrical contact with the current collector.

3. An electrode according to claim 1 or claim 2, wherein the polymeric binder is polyacrylic acid has a molecular weight greater than 50,000, eg greater than 450,000.

4. An electrode as claimed in claim 1, wherein the silicon has a purity of 95 – 99.90% by weight, e.g. 98 – 99.0% by weight:

5. An electrode as claimed in any preceding claim, wherein the binder comprises a mixture of one or more of the said polymers and another binder, e.g. an elastomer, for example carboxymethyl cellulose (CMC) and/or polyvinyldifluoride.

6. An electrode as claimed in any preceding claim, wherein the cohesive mass includes a conductivity-enhancing material, e.g. carbon black and/or acetylene black.

7. An electrode as claimed in any preceding claim, which is an anode.

8. An electrode as claimed in any preceding claim, wherein the silicon material is in the form of particles, fibres, ribbons or pillared particles.

9. An electrode as claimed in any preceding claim, wherein the silicon material comprises 20 to 100%, e.g. at least 50wt%, preferably at least 70wt% and optionally 100%, of the active material in the electrode.

10. An electrode according to any one of the preceding claims, wherein the active material further comprises active carbon selected from graphite and/or hard carbon.

11 A lithium ion cell including an electrode as claimed in any preceding claim.

12. A device including an electrode according to any one of claims 1 to 10 or a lithium ion cell according to claim 11.