(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
13 June 2024 (13.06.2024)

WIPO | PCT

(10) **International Publication Number**
WO 2024/120983 A1

(51) **International Patent Classification:**
H01M 4/50 (2010.01) ***H01M 4/60*** (2006.01)
H01M 4/52 (2010.01) ***H01M 4/62*** (2006.01)
H01M 4/525 (2010.01)

(21) **International Application Number:**
PCT/EP2023/083862

(22) **International Filing Date:**
01 December 2023 (01.12.2023)

(25) **Filing Language:** English

(26) **Publication Language:** English

(30) **Priority Data:**
2251414-5 05 December 2022 (05.12.2022) SE
2350467-3 19 April 2023 (19.04.2023) SE

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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, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, 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, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, 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, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

(54) Title: AQUEOUS CATHODE SLURRY COMPOSITION FOR CELL CATHODE

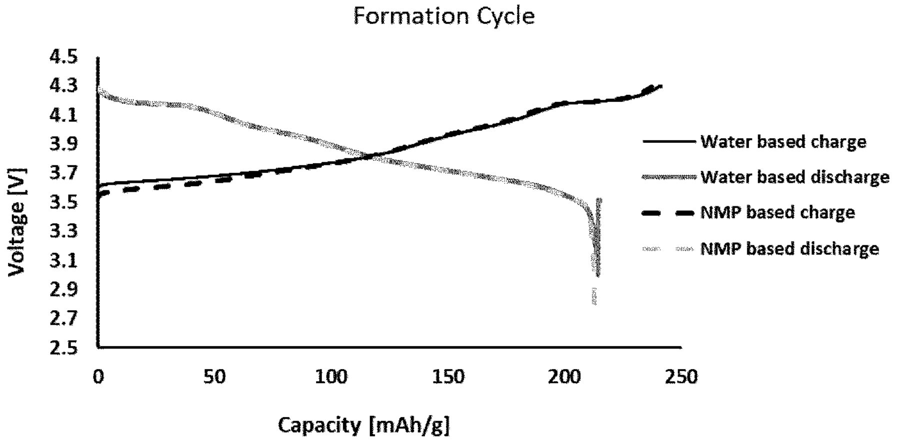

Figure 1

(57) **Abstract:** The present disclosure relates to a binder system for an electrode, a slurry composition comprising said binder composition for use in forming electrodes, and electrodes formed from the same. The binder system contains binder polymer, an alkali metal salt of an acidic polysaccharide, and an acid or salt thereof. The electrodes formed using the binder system show excellent cycle life, good flexibility and good adhesion.

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Published:

- *with international search report (Art. 21(3))*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*
- *in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE*

Aqueous cathode slurry composition for cell cathode

Field of Invention

The present invention relates to a cathode slurry composition, and its preparation, for use in a cathode, a cathode comprising the composition and a lithium-ion cell including the cathode.

Background of the Invention

There has been significant interest in the use of rechargeable batteries for use in energy storage applications. In particular, lithium-ion batteries have been widely applied in diverse industries, such as electronic devices, power tools, satellites, utility-scale storage and electric vehicles. The production of lithium-ion batteries uses considerable amounts of energy and materials, notably the amount of solvents for the production of the cathode.

Organic solvents, such as N-methyl-2-pyrrolidone (NMP), are typically used for the manufacture of cathodes in lithium-ion batteries. These organic solvents can be toxic, cause environmental damage and require complicated and expensive processing methods. Therefore, the replacement of NMP with a green, benign and cheap solvent such as water would be ideal.

Polyvinylidene fluoride (PVDF) is commonly used as a binder in cathodes in combination with NMP as the solvent. PVDF suffers from several drawbacks, such as low binding affinity, poor electrochemical and thermal stability, poor processability in water and potential toxicity. Fluorinated polymers can be harmful to both the environment and human health, and proposals are underway for the broad restriction of per- and polyfluoroalkyl substances (PFAS) in the EU. As a result, there is interest in identifying more stable, cheaper and more environmentally friendly alternatives to PVDF.

High voltage lithium-ion batteries may offer advantages such as high energy density and capacity, longer lifespan, rapid charging capability and wide compatibility with devices. High-nickel cathode materials are also commercially attractive due to the improved performance in relation to cost. However, high-nickel cathode materials are prone to adverse phase transitions, nickel leaching and deterioration in battery performance when run at high voltage. In addition, cycling under high voltage conditions may result in oxidation and/or decomposition of binder materials. Therefore, there is a need for electrodes and lithium-ion batteries with prolonged cycle stability, such as electrochemical and/or mechanical stability, which may be manufactured using an environmentally friendly process.

This disclosure relates to a novel electrode slurry composition, a method of preparation of such slurry, and electrodes and cell assemblies formed from this slurry.

Brief Description of the Invention

According to an aspect of the present disclosure, there is provided a slurry composition comprising:

a cathode active material;
a binder system;
a dispersing medium; and
optionally a conductive agent,
wherein the binder system comprises:
a binder polymer,
an alkali metal salt of an acidic polysaccharide, and
an acid or salt thereof.

According to a further aspect of the present disclosure, there is provided a method for forming a slurry composition comprising the steps of:

a. providing a composition comprising a cathode active material, an acid, an alkali metal salt of an acidic polysaccharide, a binder polymer, optionally a conductive agent, and optionally a dispersing medium; and
b. adding dispersing medium to the composition and mixing to provide a slurry composition having a solids content of from 60 wt% to 80 wt%;

provided that when the binder polymer comprises an acrylic polymer, the method comprises adding said acrylic polymer, optionally together with dispersing medium, to an intermediate slurry composition having solids content of from 65 wt% to 85 wt%, and mixing to provide a slurry composition having a solids content of from 60 wt% to 80 wt%.

According to a further aspect of the present disclosure, there is provided an electrode comprising:

a cathode active material;
a binder system; and
optionally a conductive agent,
wherein the binder system comprises:
a binder polymer,

an alkali metal salt of an acidic polysaccharide, and
an acid or salt thereof.

According to a further aspect of the present disclosure, there is provided a binder system for an electrode comprising:

a binder polymer,
an alkali metal salt of an acidic polysaccharide, and
an acid or salt thereof.

Brief description of the figures

Figure 1 shows the voltage and capacity for the half-cell of Example 1 during its formation cycle.

Figure 2 shows the voltage and capacity for the half-cell of Example 2 during its formation cycle.

Figure 3 shows the peel strength of cathodes prepared from Examples 1 to 4 and Comparative Example 1.

Figure 4 shows the peel strength of cathodes prepared from Example 1 using water or NMP as the dispersing media.

Figure 5 shows the pH of a slurry composition according to Example 2, for a period of 0 to 7 days after its preparation.

Figure 6 shows the pH of a comparative slurry composition not comprising an alkali metal salt of an acidic polysaccharide or an acid, for a period of 0 to 7 days after its preparation.

Figure 7 shows a shear rate sweep test of slurry compositions according to Example 2 using water or NMP as the dispersing media.

Figure 8 shows the gas (CO_2) evolution of slurry compositions according to Example 2 using water or NMP as the dispersing media.

The present invention will in the following be described in more detail.

Detailed Description of the Invention

Unless otherwise indicated, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention pertains.

Binder system

The present disclosure relates to slurries used to form cathodes having a particular binder system, as well as electrodes formed from the same. The binder system of the present disclosure is compatible with an aqueous dispersing media, which provides a number of processing advantages such as reduced environmental impact and cost. Furthermore, the electrode formed using the binder system has excellent properties such as flexibility, life cycle performance and rate capacity.

The binder system of the disclosure comprises a binder polymer, an alkali metal salt of an acidic polysaccharide, and an acid or salt thereof. These components combine to provide a binder system that allows cathode active materials to be processed in an aqueous media.

In some embodiments, the binder system comprises about 5 to 50 wt% of a binder polymer, about 10 to 60 wt% of an alkali metal salt of an acidic polysaccharide and about 10 to 75 wt% of an acid or salt thereof, based on the weight of the non-volatile content of the binder system.

In another embodiment, the binder system comprises about 10 to 40 wt% of a binder polymer, about 15 to 55 wt% of an alkali metal salt of an acidic polysaccharide and about 20 to 65 wt% of an acid or salt thereof, based on the weight of the non-volatile content of the binder system.

In a preferred embodiment, the binder system comprises about 10 to 40 wt% of a binder polymer, about 20 to 55 wt% of an alkali metal salt of an acidic polysaccharide and about 25 to 55 wt% of an acid or salt thereof, based on the weight of the non-volatile content of the binder system.

Preferably, the binder polymer is the binder polymer is selected from an acrylic polymer, an acrylamide copolymer or mixtures thereof.

In some embodiments, the binder system comprises about 10 to 50 wt% of an acrylamide copolymer, about 10 to 50 wt% of an alkali metal salt of an acidic polysaccharide and about 10 to 55 wt% of an acid or salt thereof, based on the weight of the non-volatile content of the binder system.

In another embodiment, the binder system comprises about 25 to 40 wt% of an acrylamide copolymer, about 15 to 30 wt% of an alkali metal salt of an acidic polysaccharide and about 20 to 50 wt% of an acid or salt thereof, based on the weight of the non-volatile content of the binder system.

In a preferred embodiment, the binder system comprises about 25 to 40 wt% of an acrylamide copolymer, about 20 to 35 wt% of an alkali metal salt of an acidic polysaccharide and about 25 to 50 wt% of an acid or salt thereof, based on the weight of the non-volatile content of the binder system.

In some embodiments, the binder system comprises about 5 to 25 wt% of an acrylic polymer, about 35 to 60 wt% of an alkali metal salt of an acidic polysaccharide and about 35 to 75 wt% of an acid or salt thereof, based on the weight of the non-volatile content of the binder system.

In another embodiment, the binder system comprises about 10 to 20 wt% of an acrylic polymer, about 40 to 55 wt% of an alkali metal salt of an acidic polysaccharide and about 40 to 65 wt% of an acid or salt thereof, based on the weight of the non-volatile content of the binder system.

In a preferred embodiment, the binder system comprises about 10 to 20 wt% of an acrylic polymer, about 40 to 50 wt% of an alkali metal salt of an acidic polysaccharide and about 45 to 55 wt% of an acid or salt thereof, based on the weight of the non-volatile content of the binder system.

The pH control of the slurry composition is important for maintaining the stability of the slurry, in addition to having a suitable viscosity for coating (and avoids corrosion of) the conductive foil (i.e. aluminium foil). Therefore, the selection of components for the binder system is critical for providing a stable and processable slurry composition which may be manufactured into a cathode. Furthermore, the resulting cathode and cell should be capable of being operated under high voltage conditions while maintaining electrochemical and/or mechanical stability.

Without wishing to be bound by theory, the acid component is believed to interact with any lithium ions that may leach from the cathode active material when it is exposed to a dispersing medium such as water. It is proposed that the acidic groups of the acid component in the binder system may react with the lithium ions of the cathode active material, which can result in a coating of the acid or salt thereof on the surface of the cathode active material. This coating may then protect the cathode active material against any further degradation. Highly acidic solutions may impact the electrode active material, and therefore an alkali metal salt of an acidic polysaccharide is used to buffer the system when in slurry form, typically to pH 6-10. The acidic polysaccharide provides the additional benefit that it can coat the electrode active material, acting as a binder as well as increasing viscosity of the slurry.

Without wishing to be bound by theory, if the cathode active material, for example a lithium NMC (nickel manganese cobalt) material, is added to the dispersing medium such as water during cathode slurry preparation, the lithium can leach out of the cathode active material and react with water, which results in the formation of hydroxide ions and an increase in the pH of the slurry. This subsequently results in the formation of LiOH and Li_2CO_3, which leads to a reduction in the capacity of the cell. Furthermore, the high pH may result in corrosion of the conductive foil. Therefore, the addition of acid to the slurry composition reduces the pH and mitigates the reaction of lithium with water and formation of unwanted by-products (see e.g. Figures 5 and 6). The acid is able to form a complex with lithium upon addition to the cathode active material during preparation of the cathode slurry composition, thereby inhibiting unwanted side reactions of lithium.

The alkali metal salt of the acidic polysaccharide is basic and acts as a buffer system. The acid and alkali metal salt of the acidic polysaccharide may react together to maintain the correct pH of the slurry composition. As a result, the pH of the slurry composition is maintained at a suitable level.

If the alkali metal salt of the acidic polysaccharide is used in the preparation of the slurry composition without any acid, lithium may react with water and form unwanted by-products. Therefore, the acid is able to balance the pH of the aqueous cathode slurry, form a complex with the lithium ions and protect degradation of the cathode active material.

The binder system additionally comprises a binder polymer which acts as a binder to the dried composition, providing flexibility and strength to the electrode formed from the slurry. The binder polymer additionally improves adhesion of the electrode to the foil. The resultant electrodes have excellent cycle life, rate capacity, as well as flexibility, allowing them to be rolled for incorporation into a cell, such as a cylindrical cell, prismatic cell, pouch cell, or coin cell.

The binder polymer in the binder provides flexibility to the final cathode, which enables rolling of the cathode during manufacture of the cell as well as better handling of cathodes during cell production/manufacture. The flexible properties are advantageous when preparing a cylindrical cell. Binders such as PVDF have typically been used in cathode slurries for lithium-ion batteries, since such compounds provide good flexibility. However, these binders contain fluorine, which may be harmful to the environment and to human health.

If the binder polymer is not added to the binder system, and the binder system contains only an alkali metal salt of an acidic polysaccharide and an acid, then this may result in a cathode which lacks flexibility. This can subsequently result in degradation of the cathode during cell operation, and poor life cycle stability.

The binder polymer also provides adhesive properties to the cathode, resulting in good adhesion of the cathode slurry composition to the conductive foil and improved peel strength. For example, a cathode comprising a binder polymer in the binder system may have a larger adhesion strength, such as peel strength, compared to a cathode that does not comprise a binder polymer. This leads to improved cycle life of the cell compared to a cathode that does not contain a binder polymer. Large volume changes of the cathode during charging and discharging under cell operation may lead to cathode delamination if there is poor adhesion between the cathode slurry composition and the conductive foil. The use of a binder polymer in the binder system prevents delamination of the cathode from the conductive foil, thereby improving cell cycle life.

For instance, the adhesion strength of an electrode to the conductive foil may be measured using a peel test. The peel strength of a cathode comprising a binder system comprising a binder polymer may be from about 10 to 120 N/m, for instance from about 30 to 110 N/m, such as from about 40 to 105 N/m, whereas a cathode comprising a binder system without a binder polymer may be from about 3 to 10 N/m. As such, the inclusion of a binder polymer in the binder system results in a cathode displaying excellent adhesion strength to the conductive foil.

When the binder polymer comprises an acrylamide copolymer, the peel strength of a cathode may be from about 35 to 60 N/m, for instance from about 45 to 50 N/m.

When the binder polymer comprises an acrylic polymer, the peel strength of a cathode may be from about 30 to 110 N/m, for instance from about 40 to 105 N/m, preferably from about 80 to 100 N/m.

In some embodiments, when the binder polymer comprises an acrylic polymer, the peel strength of a cathode may be from about 10 to 18 N/m, for instance from about 12 to 15 N/m.

The peel strength may be measured in accordance with ASTM D3330. The peel strength test may be carried out on a Universal Testing Machine (e.g. Instron 3345), for example, using an electrode sample having a width of 25 mm. Each of the electrode plates in which the coating layers were located on both surfaces of the current collectors may be cut to a size of 25 mm×150 mm. After an adhesive was coated on a glass substrate at room temperature, the electrode plate was adhered to the adhesive and roll-pressed. After one end of the electrode plate was folded 180°, a force applied to the sample was measured while pulling the sample in a direction opposite to the one end at a speed of 100 mm/min. The peel strength may be an average of 20 samples.

The binder polymer is optimal for use in the cathode of a lithium-ion cell, since it has excellent electrochemical stability during cell operation and under the conditions to which the cathode is subjected during charge and discharge cycling. Other common binder materials, such as styrene butadiene rubber (SBR), carboxymethyl cellulose (CMC), hydrogenated butadiene rubber (HBR), and other rubbers, may be suitable for use in the anode, but are incompatible for use in the cathode due to the likelihood of electrochemical oxidation if used in the cathode. For example, such binders may have poor stability when used in the electrode of a cell operating at high voltage. If a cell is run at or above 4.2 V, there may be decomposition of the binder and/or delamination of the electrode.

The binder polymer of the disclosure may provide a cathode with excellent electrochemical and/or mechanical stability, in particular when the cathode is used in a cell operated under high voltage conditions. The binder system is particularly suitable for use in high voltage cells since the cathode may retains its adhesion strength while in use (see, for example, Figures 3 and 4). A cell comprising a binder polymer, in particular wherein the cell comprises a high-nickel cathode active material, may be run under high voltage conditions without decomposition of the cell, cathode and/or binder system, while still retaining its electrochemical and/or mechanical performance, such as capacity and/or adhesion strength.

Furthermore, high-nickel cathode materials may undergo transformations under high voltage conditions, resulting in leaching of transition metals from the cathode active material (e.g. nickel and/or manganese) and/or deterioration in performance of the cell.

On the other hand, high-nickel cathode materials are considered to be promising cathode candidates due to advantages of high capacity, low cost and/or good cycle performance. In particular, high-nickel cathode materials allow for a reduced amount of cobalt (or even cobalt-free) in the cathode active material, and therefore a reduced cost. High-nickel cathode active materials may show improved capacity compared to those having a lower Ni-content. Therefore, a binder system allowing for the use of high-nickel cathode materials, for example that may be run at high voltage, while maintaining electrochemical and/or mechanical stability and/or performance, is of particular interest.

However, a high Ni content in NMC cathodes may compromise their chemical and structural stability, causing the battery to deteriorate faster than their lower Ni content counterparts. In particular, high Ni-NMC cathodes tend to evolve considerably more gas during storing than their lower Ni content counterparts.

The alkali metal salt of an acidic polysaccharide (i.e. salts of an acidic polysaccharide), for example alginates, may be particularly suitable for stabilising high-nickel cathode materials and prevent nickel and/or manganese leaching. Without wishing to be bound by theory, it is thought that the salt of an acidic polysaccharide (e.g. alginate) may bind with the nickel and/or manganese ions to form a gel, for example by producing a coating layer around the cathode active material, thereby reducing leaching of transition metals from the cathode active material. The driver for gel formation is replacement of the alkali metal cation with the divalent cation leached from the cathode active material. The binder system of the disclosure therefore provides the protective coating on the CAM where and when it is needed.

In particular, the binder system of the disclosure has also been found to reduce gas generation for cathode active materials under storage. The binder system provides particularly advantageous results when used with cathode active materials having high amounts of nickel, i.e. at 80 mol% or more nickel content. For example, the binder system of the disclosure results in decreased gas formation (see e.g. Figure 8).

Without wishing to be bound by theory, it is thought that if an alkali metal salt of an acidic polysaccharide is not used in the binder, and only binder polymer and acid are used, in particular only acrylic polymer and acid, then the pH of the aqueous cathode slurry composition during the method of its preparation is too low. This may result in the precipitation of the binder polymer (i.e. acrylic polymer), which leads to an inhomogeneous slurry that is difficult to coat onto the conductive foil, and thus a cathode with inferior properties.

The binder polymer (in particular acrylic polymer) is less stable under acidic conditions and will typically precipitate if the pH is too low. This will lead to a poorly mixed slurry composition. Therefore, the alkali metal salt of an acidic polysaccharide is required in the slurry composition in order to act as a buffer or neutralising agent and increase the pH of the slurry and prevent precipitation of the binder (i.e. acrylic) polymer.

If the slurry composition does not comprise an alkali metal salt of an acidic polysaccharide in the binder system, then this leads to a slurry composition with a pH that is too acidic. This subsequently leads to dissolution of transition metal from the cathode active material, and as a result leads to an inferior cathode and respective cell when said slurry composition is used in the cathode and cell. In particular, the cell capacity is lower for a cell comprising a cathode that is prepared using a slurry composition which is too acidic. Therefore, the alkali metal salt of the acidic polysaccharide is required in the binder system and the slurry composition in order to act as a buffer (neutralising agent) and increase the pH of the slurry composition. A slurry composition comprising the alkali metal salt of the acidic polysaccharide will result in the slurry composition being less acidic, and therefore can result in a cathode and subsequent cell comprising said cathode that displays a higher charge and discharge capacity.

Furthermore, the alkali metal salt of an acidic polysaccharide may also function as a rheological modifier in the slurry composition. This can be useful for enhancing the viscosity of the slurry, particularly when other components in the binder system have a low molecular weight. For example, if the binder system comprises an acid which has a low molecular weight, then the viscosity of the slurry can be increased by using an alkali metal salt of an acidic polysaccharide. This may subsequently be desirable for maintaining the preferred properties of the slurry composition, such as good stability and coating ability (see e.g. Figure 7).

In particular, if the cathode does not comprise an alkali metal salt of an acidic polysaccharide (i.e. alginate) in the binder system, this may result in uncontrolled leaching of transition metal (e.g. Ni and/or Mn) from the cathode active material, which may lead to an inferior cathode and respective cell while in use.

In some embodiments, the binder system is present in an amount of from about 0.2 to 8 wt%, for example about 0.5 to 6 wt%, for example about 1 to 4 wt%, for example about 1.5 to 3.5 wt%, for example about 2 to 3 wt%, based on the total weight of the dry composition (i.e. the slurry composition excluding the dispersing medium, or alternatively the electrode).

Each of these components will be described in turn.

Acid

The acid may be a molecular organic acid, a polymeric organic acid or a mineral acid.

Preferably, the acid has a pKa of from 2 to 10, more preferably from 2 to 6.

In some embodiments, the acid may comprises a molecular organic acid, such as a molecular carboxylic acid.

The acid may be a compound selected from one or more of the following malonic acid, acetic acid, citric acid, oxalic acid, formic acid, benzoic acid, carbonic acid, glycolic acid, glyoxylic acid, propanoic acid, acrylic acid, propiolic acid, lactic acid, glyceric acid, pyruvic acid, tartronic acid, mesoxalic acid, glycidic acid, butanoic acid, isobutanoic acid, succinic acid, fumaric acid, maleic acid, malic acid, tartaric acid, valeric acid, pivalic acid, glutaric acid, hexanoic acid, adipic acid, pimelic acid, salicylic acid, heptanoic acid, terephthalic acid, caprylic acid, and mixtures thereof.

Preferably, the acid is selected from malonic acid, acetic acid, citric acid, oxalic acid, gluconic acid, or mixtures thereof. More preferably, the acid is selected from malonic acid, acetic acid, citric acid, or mixtures thereof.

In some embodiments, the acid does not comprise a group 13 element, such as boron, for example boric acid and/or boronic acid.

In some embodiments, the acid may comprise a polymeric organic acid, such as a polymer comprising carboxylic acid groups.

The acid may be selected from one or more of polyacrylic acid (PAA), polymethacrylic acid (PMAA), polyethylacrylic acid, poly-4-carboxystyrene, polymaleic acid, alginic acid, carboxymethyl cellulose, and mixtures thereof.

Preferably, the acid is selected from polyacrylic acid, polymethacrylic acid (PMAA), alginic acid, carboxymethyl cellulose, or mixtures thereof. More preferably, the acid is selected from polyacrylic acid or alginic acid.

When the polymeric acid is polyacrylic acid, it may have a number average molecular weight (M_n) of from about 300,000 to about 2,000,000 g/mol, for example from about 400,000 to about 1,500,000 g/mol.

When the polymeric acid is alginic acid, it may have a number average molecular weight (M_n) of from about 10,000 to about 500,000 g/mol, for example from about 15,000 to about 300,000 g/mol.

The skilled person will understand that the molecular weight of the polymeric organic acid will affect the viscosity of a solution or a slurry containing the polymeric organic acid. A polymeric organic acid with a high molecular weight will result in a solution or a slurry with a high viscosity, which can consequently affect other properties such as the dispersion stability of the slurry and the coating ability of the slurry, when coating the cathode slurry composition onto the conductive foil. Therefore, the amount of polymeric organic acid may be varied to tune the rheological properties of the aqueous cathode slurry. The polymeric organic acid may therefore act as a rheological modifier as well as an acid in the aqueous cathode slurry.

In some embodiments, the acid may comprise a mineral acid, for example a compound selected from one or more of the following phosphoric acid, phosphonic acid, and mixtures thereof.

In some embodiments, the acid may comprise a compound containing phosphorus. For example, phosphoric acid or an organophosphorus compound, such as an organophosphate, phosphonate or an ester of phosphoric acid.

Suitable examples include a compound selected from one or more of the following H_3PO_4, H_2RPO_4, HR_2PO_4, $HRR'PO_4$, and mixtures thereof, wherein R and R′ represent organic groups.

Preferably, the acid is phosphoric acid.

The acid is preferably selected from one or more of malonic acid, acetic acid, citric acid, oxalic acid, polyacrylic acid, alginic acid, carboxymethyl cellulose, phosphoric acid, and mixtures thereof.

More preferably, the acid is selected from one or more of malonic acid, acetic acid, citric acid, polyacrylic acid, alginic acid, phosphoric acid, and mixtures thereof.

The amount of acid in the composition depends on the pKa value of the acid. If the acid has a high pKa value, for example if the acid is weak, then more acid may be required to reduce the pH of the slurry composition. If the acid has a low pKa value, for example if the acid is strong, then less acid may be needed to reduce the pH of the slurry composition.

The acid may be present in an amount of from about 0.03 to about 5 wt%, such as from about 0.05 to about 4 wt%, for example from about 0.05 to about 2 wt%, for example from about 0.1 to about 3 wt%, preferably from about 0.2 to about 1 wt% based on the total weight of the dry composition (i.e. the slurry composition excluding the dispersing medium, or alternatively the electrode).

The acid may be present in the system in the form of its salt, which is typically formed by reaction with lithium or by reaction with the alkali metal salt of the acidic polysaccharide.

The salt of the acid is therefore typically an alkali metal salt, such as a lithium or sodium salt, preferably a lithium salt.

Alkali metal salt of acidic polysaccharide

An “acidic polysaccharide” is a polysaccharide having carboxyl groups.

In one embodiment, the acidic polysaccharide is a compound selected from one or more of alginic acid, xanthan gum, and combinations thereof.

Preferably, the acidic polysaccharide is alginic acid.

The acidic polysaccharide has a molecular weight that allows coating of the cathode active material, yet is not so high that the viscosity of the slurry composition becomes too high to allow the composition to be coated onto a foil.

Typical number average molecular weights (M_n) are from about 10,000 to about 500,000 g/mol, for example from about 15,000 to about 300,000 g/mol, based on the acid (i.e. not the alkali metal salt of the acid polysaccharide)

When the acidic polysaccharide is alginic acid, it may have a number average molecular weight (M_n) of from about 10,000 to about 500,000 g/mol, for example from about 15,000 to about 300,000 g/mol, based on the acid (i.e. not the alkali metal salt of the acid polysaccharide).

The acidic polysaccharide is present as an alkali metal salt. The acidic groups in the acidic polysaccharide are preferably all in salt form, i.e. the acidic polysaccharide preferably does not contain any free acid groups.

The alkali metal may be selected from lithium, sodium, potassium, or mixtures thereof. Preferably, the alkali metal is selected from lithium or sodium.

Preferably, the alkali metal salt of an acidic polysaccharide is selected from lithium alginate, sodium alginate, or a combination thereof.

It has been found that lithium and sodium alginate provide several desirable properties. Lithium and sodium alginates have good solubility in water, can act as rheological modifiers and can also act as buffering agents which can balance the pH of the slurry composition. Therefore, lithium alginate or sodium alginate may act both as a viscosity modifier and a neutralising agent.

Lithium and sodium alginate are therefore preferable over other alkali metal salts of acidic polysaccharides since they may enhance the viscosity of the slurry composition and act as a neutralising agent. Other acidic polysaccharides, such as sodium carboxymethyl cellulose, may only form neutral or weakly alkaline solutions and therefore cannot act effectively as neutralising agents, whereas lithium and sodium alginate form more alkaline solutions and therefore are more effective as neutralising agents.

Acidic polysaccharides are a good material to use since they are relatively low cost and are often sourced from natural products. Furthermore, they are also biodegradable. Alginates or alginic acid also provide good properties in the final electrode, since they can have a supramolecular self-healing ability which allows them to accommodate large volume changes of the electrode (which may occur during charge and discharge cycling). This ability prevents the electrode from cracking, or losing contact with other cell components, during charge and discharge cycling when used in the cell. As a result, the cell capacity may be retained during cell usage.

In some embodiments, some (or all) of the alkali metal salt of an acidic polysaccharide may be in the form of a metal salt of an acidic polysaccharide (e.g. a transition metal salt of an acidic polysaccharide), for example due to reaction with the cathode active material (e.g. the transition metal).

The alkali metal salt of an acidic polysaccharide may be present in an amount of from about 0.01 to about 3 wt%, such as from about 0.03 to about 2 wt%, for example from about 0.05 to about 1 wt%, preferably from about 0.5 to about 1 wt%, based on the total weight of the dry composition (i.e. the slurry composition excluding the dispersing medium, or alternatively the electrode).

The alkali metal salt of acidic polysaccharide may be soluble in a solvent, such as water. For example, the alkali metal salt of acidic polysaccharide may be a water-soluble alkali metal salt of acidic polysaccharide.

The alkali metal salt of the acidic polysaccharide may be formed by reacting an acidic polysaccharide with a suitable alkali metal hydroxide, such as lithium hydroxide or sodium hydroxide, in a solvent such as water.

Binder polymer

The binder polymer provides flexibility to the electrode, improves adhesion of the electrode to the foil, and reduces unwanted side reactions in the slurry prior to formation of the electrode.

In some embodiments, the binder polymer is present in an amount of from about 0.05-5 wt%, such as from about 0.1-4 wt%, for example from about 0.1-3 wt%, such as about 0.1-1.5 wt%, for example from about 0.1-0.7 wt%, based on the total weight of the dry composition (i.e. the slurry composition excluding the dispersing medium, or alternatively the electrode).

In one embodiment the binder polymer has a number average molecular weight (M_n) of from about 300,000-2,000,000 g/mol, for example from about 400,000-1,500,000 g/mol. Preferably, the number average molecular weight is between 500,000-1,000,000 g/mol, for example between 600,000-900,000 g/mol.

The binder polymer typically has a pH (when dispersed in water) of from 5-10, for example from 6-10, preferably from 7-9.

The binder polymer, particularly an acrylic polymer, may have a glass transition temperature of from about -80 to about 65 °C, for example from about -60 to about 45 °C, such as from about -40 to about 25 °C. A glass transition temperature within this range may help to improve the electrode flexibility, which can subsequently lead to better cycle life performance and rate capacity of the cell.

Preferably, the binder polymer comprises or consists of an acrylic polymer, an acrylamide copolymer, or a mixture thereof.

By "acrylamide copolymer" is meant a polyacrylamide copolymer, or in other words a polymer formed from different monomers wherein one of the monomers is chosen from the group of acrylamide monomer.

The acrylamide monomer may be selected from one or more of the following acrylamide, methacrylamide, or mixtures thereof.

Preferably, the acrylamide copolymer comprises 20-80 wt% (meth)acrylamide.

By "(meth)acrylamide" is meant acrylamide or methacrylamide, i.e. the parenthesis indicate that the methyl group may or may not be present.

The acrylamide copolymer typically comprises (meth)acrylamide and at least one acidic comonomer, preferably (meth)acrylamide and at least one comonomer selected from a carboxylic acid, a sulfonic acid, or mixtures thereof.

The acrylamide copolymer thus typically further comprises the inclusion of monomers of unsaturated organic acids selected from the group consisting of unsaturated carboxylic acids and unsaturated sulfonic acids and/or the alkali metal salt thereof.

Examples of unsaturated carboxylic acids include (meth)acrylic acid, crotonic acid, maleic acid, fumaric acid and itaconic acid.

Examples of unsaturated sulfonic acids include α,ß-ethylenically unsaturated sulfonic acid, such as vinylsulfonic acid, styrenesulfonic acid, (meth)allylsulfonic acid; meth)acrylamide t-butylsulfonic acid, 2-(meth)acrylamide-2-methylpropanesulfonic acid, 2-(meth)acrylamide-2-hydroxypropanesulfonic acid, 3-sulfopropane(meth)acrylic ester, and bis-(3-sulfopropyl)itaconic ester.

Preferred unsaturated acid monomers include (meth)acrylic acid and (meth)allyl sulfonic acid.

Preferably, the acrylamide copolymer comprises 5-50 wt% unsaturated organic acids and/or the alkali metal salt thereof, more preferably from 10 to 40 wt%.

The acid component is typically present in a mixture of the acid and alkali metal salt form, for instance wherein from 20% to 80% of the acid groups are present as the alkali metal salt, preferably from 25% to 75%.

Suitable alkali metals are selected from lithium, sodium or potassium, with lithium and sodium being preferred and lithium being particularly preferred.

Optionally, the acrylamide copolymer comprises the inclusion of monomers of hydroxyl group containing vinyl compounds. For example, the hydroxyl group containing vinyl compound may be a hydroxyl containing vinyl ether.

Optionally, the acrylamide copolymer comprises 0-75 wt% hydroxyl group containing vinyl compounds.

In some embodiments, the acrylamide copolymer is delivered as an aqueous solution comprising from 10 to 15 wt% acrylamide copolymer. Preferably, the acrylamide copolymer content in the aqueous solution is from 13 to 14 wt%, such as approximately 13.5 wt%.

In an embodiment, the acrylamide copolymer preferably has a pH (in water) from 5 to 10. Preferably, from 7 to 9. For example, the pH of the acrylamide copolymer can be altered by varying the amount of acid and metal salt thereof.

In some embodiments, the acrylamide copolymer in an aqueous solution has a viscosity from 10,000-30,000 mPa·s, for example from 15,000-25,000 mPa·s, preferably from 17,000-23,000 mPa·s.

The viscosity is measured by a B-type viscometer such as "B-type Viscometer Model BM" (product name) by Toki Sangyo Co., Ltd. Preferably, the acrylamide copolymer content in the aqueous solution is approximately 13.5 wt% during viscosity measurement.

In one embodiment the acrylamide copolymer has a number average molecular weight (M_n) of from about 300,000-2,000,000 g/mol, for example from about 400,000-1,500,000 g/mol, such as between 500,000-1,000,000 g/mol, for example between 600,000-900,000 g/mol.

In some embodiments, the acrylamide copolymer is present in an amount of from about 0.05-5 wt%, for example from about 0.05-2 wt%, such as from about 0.1 to about 1 wt%, preferably about 0.1 to about 0.7 wt%, based on the total weight of the dry composition (i.e. the slurry composition excluding the dispersing medium, or alternatively the electrode).

Preferably, the binder polymer, in particular the acrylic polymer, is in the form of a non-ionic polymer and/or non-acidic polymer. For example, preferably the acrylic polymer does not comprise free acid groups, such as carboxylic acid groups. In this way, the pH of the slurry composition does not become too acidic, thereby avoiding dissolution of transition metal from the cathode active material and/or precipitation of components of the slurry.

By "acrylic polymer" is meant a polyacrylate polymer, or in other words a polymer formed from acrylic acid alkyl ester monomers, for example an acrylate alkyl ester monomer. Preferably, the acrylic polymer is a polyacrylate polymer wherein the acrylic groups are in the form of esters. For example, wherein the acrylic polymer does not comprise an acidic group, such as a carboxylic acid group.

The acrylic polymer may be selected from one or more of the following poly(methyl methacrylate), poly(methyl acrylate), poly(ethyl acrylate), poly(butyl acrylate), poly(2-ethylhexyl acrylate), and mixtures thereof.

The acrylic polymer may be a copolymer formed from two or more of methyl methacrylate, methyl acrylate, ethyl acrylate, butyl acrylate, or 2-ethylhexyl acrylate.

The acrylic polymer typically has a pH (when dispersed in water) of from 6 to 10, for example from 6 to 9 and preferably from 8 to 9.

In one embodiment. the acrylic polymer has a number average molecular weight (M_n) of from about 300,000 to about 2,000,000 g/mol, for example from about 400,000 to about 1,500,000 g/mol.

In some embodiments, the acrylic polymer is present in an amount of from about 0.05- to about 5 wt%, such as from about 0.1 to about 4 wt%, for example from about 0.2 to about 3 wt%, preferably about 0.5 to about 1.5 wt%, based on the total weight of the dry composition (i.e. the slurry composition excluding the dispersing medium, or alternatively the electrode).

Dispersing medium

The slurry composition comprises a dispersing medium.

The dispersing media may include N-methyl pyrrolidone (NMP), water, or mixtures thereof.

Preferably, the dispersing medium comprises water. Other solvents may also be used in combination with water, such as organic solvents that are miscible with water may be used.

More preferably, the dispersing medium consists of water.

The use of aqueous solvents is preferred, since this can help to reduce costs by avoiding the use of a humidity-controlled environment and dry room conditions during cathode manufacture. Furthermore, the cost of the aqueous solvent itself may be cheaper compared to solvents such as NMP.

Cathode active material

The cathode active material may comprise a suitable material for use as an electrochemically active material in the cathode of a cell, particularly a lithium ion cell.

The term "electrochemically active material" is to be understood as an electrochemical species which can be oxidised and reduced in a system which enables a cell to produce electric energy during discharge. The role of the cathode active material is to reversibly store, convert and/or alloy with lithium, e.g. via intercalation (or otherwise binding) ions (such as lithium ions) during cell charge and discharge cycles.

The cathode active material may comprise an intercalation material, such as a lithium intercalation material, for example a lithium metal oxide which may include lithium and a transition metal.

The cathode active material may comprise any one or a mixture of two or more of lithium manganese oxide, lithium nickel oxide, lithium cobalt oxide, lithium nickel manganese oxide (LNMO), lithium nickel cobalt oxide, lithium nickel manganese cobalt (NMC) oxide, lithium iron phosphate (LFP), lithium nickel manganese phosphate (NiMP), lithium iron manganese phosphate (LFMP) and lithium nickel cobalt aluminium oxide (NCA).

Desirably, the cathode active material may comprise any one or a mixture of two or more of lithium manganese oxide, lithium nickel oxide, lithium cobalt oxide, lithium nickel manganese oxide (LNMO), lithium nickel cobalt oxide, lithium nickel manganese cobalt (NMC) oxide, lithium iron phosphate (LFP), lithium iron manganese phosphate (LFMP) and lithium nickel cobalt aluminium oxide (NCA).

Preferably, the cathode active material is an NMC material, i.e. a lithium nickel manganese cobalt oxide. Even more preferably, the cathode active material is an NMC material intercalated with lithium or an "Li-NMC" material.

The cathode active material may comprise 80 mol% or more Ni, based on the total amount of non-lithium metals in the cathode active material, such as from about 80-98 mol% Ni, for example from about 90-95 mol% Ni, such as from about 85-95 mol% Ni, such as from about 88-92 mol% Ni, based on the total amount of non-lithium metals in the cathode active material.

Exemplary cathode active materials include nickel-manganese-cobalt (NMC) composite oxides and lithium NMC (Li-NMC) composite oxides or lithium nickel manganese cobalt (NMC) oxides ($LiNi_{1-x-y}Co_xMn_yO_2$ ($0<x+y\leq0.2$)).

In some embodiments, the cathode active material may comprise lithium nickel cobalt manganese oxides (NMC) ($Li_bNi_{1-x-y-z}Co_xMn_yA_zO_2$ ($0<x+y+z\leq0.2$)), where A is an element other than Li, Ni, Co, Mn or O and wherein $0\leq z\leq0.05$, preferably $0<z\leq0.03$, more preferably $0.001<z\leq0.01$, and wherein $0.9\leq b\leq1.2$. A is one or more chosen from the group Al, B, Zr, Ba, Ca, Ti, Mg, Ta, Nb, V, Fe, Ru, Re, Pt and Mo. Preferably, A is chosen from the group Al and Zr.

In preferred embodiments, the NMC cathode materials may be defined as $Li_bNi_{1-x-y-z}Co_xMn_yA_zO_2$, wherein $0<x+y+z\leq0.2$, preferably $0<x+y+z\leq0.15$, more preferably $0<x+y+z\leq0.12$, and wherein $0\leq z\leq0.05$, preferably $0.002\leq z\leq0.03$, more preferably $0.001<z\leq0.01$, and wherein $0.9\leq b\leq1.1$. A is one or more chosen from the group Al, B, Zr, Ba, Ca, Ti, Mg, Ta, Nb, V, Fe, Ru, Re, Pt and Mo. Preferably, A is chosen from the group Al and Zr.

The cathode active material may comprise a lithium metal oxide material that is coated with another material. For example, a lithium metal oxide may be coated with a different lithium metal oxide, carbon, graphene, or a combination thereof. Furthermore, the coating material may have been coated using atomic layer deposition (ALD) as a non-limiting example.

The cathode active material may be present in an amount of from about 80 to about 99 wt%, for example from about 85 to about 99 wt%, such as from about 90 wt% to about 98 wt%, for example from about 95 to about 97 wt%, based on the total weight of the dry composition (i.e. the slurry composition excluding the dispersing medium, or alternatively the electrode).

Conductive agent

The role of the conductive agent is to improve the electronic properties of the cathode and to provide an electrical connection between the particles of cathode active material in the cathode. As it is present merely to improve conductivity, it is optional as the inherent conductivity of the cathode active material may be sufficient.

For example, the conductive agent may comprise carbon black, acetylene black, graphene, graphite, mesocarbon microbead (MCMB), pitch-based carbon, coke powders, single-walled, thin-walled and/or multi-walled carbon nanotubes, metallic powders, or a combination thereof.

Preferred conductive agents are selected from carbon black, acetylene black, carbon nanotubes, or a combination thereof.

In an embodiment, the conductive agent may be present in an amount of from about 0 wt% to about 6 wt%, for example from 0 wt% to about 4 wt%, such as from about 0 wt% to about 3 wt%, preferably from about 0.1 wt% to 2 wt%, or from about 0.3 wt% to 2 wt%, based on the total weight of the dry composition (i.e. the slurry composition excluding the dispersing medium, or alternatively the electrode).

Slurry composition

The slurry composition is formulated to a suitable viscosity to allow it to be processed into a cathode, for example by slot-die coating. For example, the slurry composition may display a shear-thinning non-Newtonian behaviour.

The slurry composition typically has a dynamic viscosity of from about 0.5-50 Pa.s at a shear rate of about 10 s^{-1}, such as from about 1-40 Pa.s, for instance from about 2 to about 40 Pa.s, for instance from about 2-25 Pa.s, as measured at 25°C.

The slurry composition typically contains from about 60 to 80 wt% solids, such as from about 65 to 75 wt% solids, preferably from about 68 to 73 wt% solids, more preferably from about 70 to 72 wt% solids, with the remainder being dispersing medium.

The method of formation of the slurry composition is not critical, and once formed it is typically stable at room temperature for at least one day, preferably at least one week. By "stable" in this context is meant that the solid particles do not settle.

The components of the binder system (i.e. the binder polymer, alkali metal salt of an acidic polysaccharide and acid or salt thereof) may be added at different steps during the preparation of the slurry composition.

While it may be possible to form the slurry composition by combining the ingredients in any order, best results are obtained when following the method of the disclosure which comprises the steps of:

a. providing a composition comprising cathode active material, an acid, an alkali metal salt of an acidic polysaccharide, a binder polymer, optionally a conductive agent, and optionally a dispersing medium;
b. adding dispersing medium to the composition and mixing to provide a slurry composition having a solids content of from 60 wt% to 80 wt%;

provided that when the binder polymer comprises acrylic polymer, the method comprises adding said acrylic polymer, optionally together with dispersing medium, to an intermediate slurry composition having a solids content of from 65 wt% to 85 wt%, and mixing to provide a slurry composition having a solids content of from 60 wt% to 80 wt%.

The intermediate slurry composition is prepared by adding dispersing medium to the composition of step a. and mixing.

The cathode active material and conductive agent may be dry mixed. However, the conductive agent (when present) is typically provided as a dispersion to aid in its processing. The first mixing step may therefore have small amounts of dispersing medium, which is typically water.

Likewise, the acid and/or alkali metal salt of acidic polysaccharide may also be provided as dispersions, to aid in their processing.

Typically, the binder polymer is added as a dispersion to aid in its mixing into the composition.

Typically, the composition has a pH of from 5 to 8 after step a., for instance from about pH 6 to 7.

The addition of dispersing medium is typically done stepwise, but may be continuous. The overall process is typically done at a rate which ensures even and thorough mixing of the dispersing medium into the composition. During this step, the alkali metal salt of the acidic polysaccharide may begin to coat the cathode active material.

The pH of the composition after step b. is typically from pH 6 to 10, for instance from about pH 6 to 8 or from pH 6 to 7. In some embodiments, the pH of the composition after step b. may be 7 to 10, for example from pH 7.5 to 9, preferably from pH 8 to 9.

In the case of preparing the slurry composition wherein the binder polymer is an acrylamide copolymer, best results are obtained when following the method of the disclosure which comprises the steps of:

1. providing a composition comprising cathode active material, acrylamide copolymer, an acid, an alkali metal salt of an acidic polysaccharide, optionally a conductive agent, and optionally a dispersing medium;

2. adding dispersing medium to the composition and mixing to provide a slurry composition having a solids content of from 60 wt% to 80 wt%.

Step 1. of the method comprises forming a mixture of cathode active material, acrylamide copolymer, (optional) conductive agent, acid and alkali metal salt of acidic polysaccharide. These agents may be combined in any order, and may be dry mixed.

Typically, step 1. comprises:

forming a mixture of cathode active material and optional conductive agent;

adding acrylamide copolymer, acid and alkali metal salt of acidic polysaccharide and mixing, optionally in the presence of a dispersing medium.

The cathode active material and conductive agent may be dry mixed. However, the conductive agent (when present) is typically provided as a dispersion to aid in its processing. The first mixing step may therefore have small amounts of dispersing medium, which is typically water.

Likewise, the acid and/or alkali metal salt of acidic polysaccharide may also be provided as dispersions, to aid in their processing.

Typically, the acrylamide copolymer is added as a dispersion to aid in its mixing into the composition.

In view of this, step 1. typically comprises providing a composition comprising cathode active material, acrylamide copolymer, an acid, an alkali metal salt of an acidic polysaccharide, a dispersing medium, and optionally a conductive agent, said composition having above 85 wt% solid content.

Typically, the composition has a pH of from 5 to 8 after step a., for instance from about pH 6 to 7.

Step 2. comprises adding dispersing medium and mixing to decrease the solids content of the composition. During this step, the composition transitions through a clay-like solid to a free-flowing slurry having a solids content of from 60 to 80 wt%.

The addition of dispersing medium is typically done stepwise but may be continuous. The overall process is typically done at a rate which ensures even and thorough mixing of the dispersing medium into the composition. During this step, the alkali metal salt of the acidic polysaccharide may begin to coat the cathode active material.

The pH of the slurry composition after step 2. is typically from pH 6 to 10, for instance from pH 7 to 10, for example from pH 7.5 to 9, preferably from pH 8 to 9.

In the case of preparing the slurry composition wherein the binder polymer is an acrylic polymer, best results are obtained when following the method of the disclosure which comprises the steps of:

i. providing a composition comprising cathode active material, an acid, an alkali metal salt of an acidic polysaccharide, optionally a conductive agent, and optionally a dispersing medium;
ii. adding dispersing medium to the composition and mixing to provide an intermediate slurry composition having a solids content of from 65 wt% to 85 wt%; and
iii. adding an acrylic polymer and optionally dispersing medium to the intermediate slurry composition to provide a slurry composition having a solids content of from 60 wt% to 80 wt%.

Step i. of the method comprises forming a mixture of cathode active material, (optional) conductive agent, acid and alkali metal salt of acidic polysaccharide. These agents may be combined in any order, and may be dry mixed.

Typically, step i. comprises:

forming a mixture of cathode active material and optional conductive agent;

adding acid and alkali metal salt of acidic polysaccharide and mixing, optionally in the presence of a dispersing medium.

The cathode active material and conductive agent may be dry mixed. However, the conductive agent (when present) is typically provided as a dispersion to aid in its processing. The first mixing step may therefore have small amounts of dispersing medium, which is typically water.

Likewise, the acid and/or alkali metal salt of acidic polysaccharide may also be provided as dispersions, to aid in their processing. In view of this, step i. typically comprises providing a composition comprising cathode active material, an acid, an alkali metal salt of an acidic polysaccharide, a dispersing medium, and optionally a conductive agent, said composition having above 85 wt% solid content.

Typically, the composition has a pH of from 5 to 8 after step i., for instance from about pH 6 to 7.

Step ii. comprises adding dispersing medium and mixing to decrease the solids content of the composition. During this step, the composition transitions through a clay-like solid to a free-flowing slurry.

The addition of dispersing medium is typically done stepwise, but may be continuous. The overall process is typically done at a rate which ensures even and thorough mixing of the dispersing medium into the composition. During this step, the alkali metal salt of the acidic polysaccharide may begin to coat the cathode active material.

The pH of the composition after step ii. is typically from pH 6 to 8, for instance from about pH 6 to 7.

Step iii. comprises adding the acrylic polymer typically with dispersing medium under mixing to provide the final slurry composition.

Typically, the acrylic polymer is added as a dispersion to aid in its mixing into the composition.

The pH of the slurry composition after step c. is typically from pH 6 to 10, for instance from pH 7 to 10, for example from pH 7.5 to 9, preferably from pH 8 to 9.

Adding the acrylic polymer too early in the process may lead to poor coating properties and formation of bubbles. Additionally, if the acrylic polymer is exposed to very low pH compositions, it may precipitate resulting in poor integration into the slurry composition.

Preferably, the slurry composition comprises at least 90 wt% cathode active material, based on the total weight of the dry composition (i.e. the slurry composition excluding the dispersing medium, or alternatively the electrode).

The slurry composition may be used to form a cathode in a cell using standard methodologies, such as by slot-die coating a conductive foil and drying the composition to form a cathode.

The cathode according to the disclosure (i.e. those containing the binder system of the disclosure, or formed from the slurry composition of the disclosure) display improved cycle life, good flexibility, and good adhesion to the conductive foil.

The remaining features of the cell of the disclosure will be briefly described.

Conductive foil

The cell of the disclosure may comprise a first and second conductive foil. Said current foils act as one of a cathode or an anode current collector.

In a preferred embodiment, the first conductive foil acts as the cathode current collector and the second conductive foil acts as the anode current collector.

The cathode current collector may comprise a metal, such as aluminium, nickel or stainless steel. Preferably, the positive current collector is an aluminium foil.

The anode current collector may comprise a metal, such as copper, nickel or stainless steel. Preferably, the negative current collector is a copper foil.

The conductive foil may have a coating such as a carbon coating, which can improve conductivity at the interface with the electrode active material. The coating may also improve the peel strength (or adhesive properties) of layers coated thereon, reducing delamination of the electrode.

Anode

The cell may comprise an anode. The anode may comprise an anode active material, such as metallic lithium, lithium/aluminium alloys, lithium/tin alloys, carbon, graphite, black lead, silicon, silicon/silicon composite, or a combination thereof. The anode may further comprise a conductive agent and a binder.

The role of the anode active material is to reversibly bind the lithium. The mechanism of binding will vary, and may be by intercalation/deintercalation (for instance with graphite), alloying/dealloying (for instance with silicon), or by plating/stripping (for instance with metallic lithium), or combinations thereof.

Preferably, the anode comprises carbon and/or silicon.

Suitable anode active materials are selected from silicon, SiOx, silicon-carbon composites, prelithiated silicon or its composites and oxides.

The anode active material, conductive agent and binder may be coated on the second conductive foil (e.g. the copper foil). The anode active material, conductive agent and binder may be coated on the inner and outer sides of the second conductive foil.

Electrolyte

The cell of the disclosure further comprises an electrolyte. The electrolyte used in the cell according to the present disclosure may be a liquid electrolyte comprising at least one salt (particularly at least one lithium salt) and at least one or more solvents selected from the group consisting of carbonate solvents and their fluorinated equivalents, diC1-4 ethers and their fluorinated equivalents and ionic liquids. Alternatively, the electrolyte may be a solid electrolyte.

The lithium salt is preferably one or more selected from the group consisting of lithium hexafluorophosphate ($LiPF_6$), lithium bis(fluorosulfonyl)imide (LiFSI), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), lithium (fluorosulfonyl)(trifluoromethanesulfonyl)imide (LiFTFSI), lithium bis(pentafluoroethanesulfonyl)imide (LiBETI), lithium (pentafluoroethanesulfonyl)(trifluoromethanesulfonyl)imide (LiPTFSI), lithium trifluoromethanesulfonate (LiOTf), lithium bis(oxalato)borate (LiBOB), lithium difluoro(oxalato)borate (LiDFOB), lithium difluorobis(oxalato)phosphate (LiDFOP), lithium tetrafluoro(oxalato)phosphate (LiTFOP), lithium tetrafluoroborate ($LiBF_4$), lithium nitrate ($LiNO_3$) lithium 2-trifluoromethyl-4,5-dicyanoimidazole (LiTDI).

In one embodiment, the solvent is selected from the group consisting of 1,2-dimethoxyethane (DME), N-propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide (PYR13-FSI), N-propyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR13-TFSI), 1-butyl-1-methylpyrrolidinium bis(fluorosulfonyl)imide (PYR14-FSI), 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR14-TFSI), 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)imide (EMIM-FSI), 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMIM-TFSI), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC), ethylene carbonate (EC), and propylene carbonate (PC), and their fluorinated equivalents.

Separator

The cell of the disclosure may comprise one or more separators disposed between the anode and the cathode. The function of these separators is to prevent electrical contact between the cathode and the anode, whilst allowing the passage of ions. Any separator suitable for use in a cylindrical/pouch/prismatic/coin(e.g. lithium-ion) cell may be used.

For example, the separator may be made from a material such as glass fiber, polyester, Teflon, polyethylene, polypropylene, polytetrafluoroethylene (PTFE), or a combination thereof, and may be in the form of a nonwoven fabric or a woven fabric.

Optionally the separator is an integrated separator. For example, the separator may be integrated with a composite electrode to form an integrated electrode-separator (IES).

Cell

The cell may include at least a cathode, an anode and an electrolyte, wherein the cathode comprises the binder system described herein. The cell may include a separator.

The cell may be a cylindrical, prismatic, coin cell or pouch cell.

The cell may be a lithium-ion cell, such as a secondary lithium-ion cell.

Preferably, the cell is a cylindrical secondary lithium-ion cell.

The cell may be combined with other cells to form a battery system (i.e. an array of cells).

The disclosure also relates to a vehicle comprising the cell and/or battery system of the disclosure. The vehicle is preferably an electric vehicle, such as a car, truck, bus, scooter, motorbike, bicycle, boat, plane or the like, preferably a car, truck or bus.

The embodiments of the disclosure will be further described in the following non-limiting examples:

Examples

Example 1

A coin half-cell was prepared using a cathode formed from the slurry composition described herein. Slurry compositions were prepared using either water or NMP as dispersing media. A nickel rich NMC cathode active material was used as cathode active material. Malonic acid was used as the acid, and sodium alginate was used as the alkali metal salt of an acidic polysaccharide in the binder system. An acrylamide copolymer was used as the binder polymer.

The slurry composition comprised from about 90 to 98 wt% cathode active material, from about 0 to about 3 wt% conductive agent, from about 0.05 to 2 wt% acid or salt thereof, from about 0.1 to 3 wt% alkali metal salt of an acidic polysaccharide and from about 1 to 5 wt% acrylamide copolymer, based on the total weight of the dry composition (i.e. the slurry composition excluding the dispersing medium, or alternatively the electrode).

The anode used in the coin half-cell was lithium. A ceramic-coated separator was used to separate the anode and cathode. Stainless steel was used for the positive and negative casing elements of the cell. The formation cycle results of the coin half-cell prepared using the water-based slurry composition were similar to the coin half-cell prepared using an NMP-based slurry composition (Table 1).

Table 1. Formation (initial) cycle results for coin half-cells prepared using either an NMP-based cathode slurry or a water-based cathode slurry.

Formation cycle (coin half-cell)			
Cathode slurry type	**Charge capacity (mAh/g)**	**Discharge capacity (mAh/g)**	**Initial Coulombic Efficiency (%)**
NMP-based	237.41	212.65	89.57
Water-based	241.5563	215.23	89.10

The voltage vs. capacity for the formation cycle of the coin half-cell is shown in Figure 1. The Figure shows a difference in properties of the electrodes formed from either water or NMP during the charge cycle, with similar properties on the discharge cycle.

The direct current internal resistance (DCIR) was measured at 100% state of charge. A low value indicates that a large current can be delivered with minimal voltage drop. The DCIR results of the coin half-cell prepared using the water-based slurry composition were similar to the coin half-cell prepared using an NMP-based slurry composition (Table 2).

Table 2. Direct current internal resistance

Cathode slurry type	Resistance (Ohm)
NMP-based	9.00
Water-based	8.85

Example 2

A coin half-cell was prepared using a cathode formed from the slurry composition described herein. Slurry compositions were prepared using either water or NMP as dispersing media. Malonic acid was used as the acid and sodium alginate was used as the alkali metal salt of an acidic polysaccharide in the binder system. An acrylic polymer was used as the binder polymer.

The slurry composition comprised from about 95 to 99 wt% cathode active material, from about 0 to about 3 wt% conductive agent, from about 0.4 to 5 wt% acid or salt thereof, from about 0.1 to 3 wt% alkali metal salt of an acidic polysaccharide and from about 0.4 to 5 wt% acrylic polymer, based on the total weight of the dry composition (i.e. the slurry composition excluding the dispersing medium, or alternatively the electrode).

The anode used in the coin half-cell was lithium. A ceramic-coated separator from celgard was used to separate the anode and cathode. Stainless steel was used for the positive and negative casing elements of the cell. The formation cycle results of the coin half-cell prepared using the water-based slurry composition were similar to the coin half-cell prepared using an NMP-based slurry composition (Table 3).

Table 3. Formation (initial) cycle results for coin half-cells prepared using either an NMP-based cathode slurry or a water-based cathode slurry.

Formation cycle (coin half-cell)			
Cathode slurry type	**Charge capacity (mAh/g)**	**Discharge capacity (mAh/g)**	**Initial Coulombic Efficiency (%)**
NMP-based	240.6	213.7	88.82
Water-based	240.911	214.23	88.92

The voltage vs. capacity for the formation cycle of the coin half-cell is shown in Figure 2. The Figure shows a difference in properties of the electrodes formed from either water or NMP during the charge cycle, with merged properties on the discharge cycle.

The coin half-cell prepared using the water-based cathode slurry composition displayed better capacity retention after 50 cycles (1C/1C) compared to the coin half-cell prepared using the NMP-based cathode slurry composition (Table 4).

Table 4. Capacity retention of coin half-cells prepared using either an NMP-based cathode slurry or a water-based cathode slurry after 50 cycles.

Capacity retention after 50 cycles at 25 °C (coin half-cell)	
Cathode slurry type	**Discharge capacity retention (%)**
NMP-based	95.80%
Water-based	95.90%

Example 3

A cathode was prepared from the slurry composition described herein using water as dispersing media. A high-nickel NMC cathode active material was used as cathode active material comprising from about 90 to 95 mol% Ni, from about 1 to 5 mol% Mn and from about 0 to 5 mol% Co, based on the total amount of non-lithium metals in the cathode active material.

Malonic acid was used as the acid, and sodium alginate was used as the alkali metal salt of an acidic polysaccharide in the binder system. An acrylamide copolymer was used as the binder polymer.

The slurry composition comprised from about 90 to 98 wt% cathode active material, from about 0 to about 3 wt% conductive agent, from about 0.05 to 2 wt% acid or salt thereof, from about 0.1 to 3 wt% alkali metal salt of an acidic polysaccharide and from about 1 to 5 wt% acrylamide copolymer, based on the total weight of the dry composition (i.e. the slurry composition excluding the dispersing medium, or alternatively the electrode).

The peel strength of a cathode prepared with Example 3 is shown in Figure 3.

Example 4

A cathode was prepared from the slurry composition described herein using water as dispersing media. A high-nickel NiMP cathode active material was used as cathode active material comprising from about 85 to 95 mol% Ni and from about 1 to 20 mol% Mn, based on the total amount of non-lithium metals in the cathode active material.

Malonic acid was used as the acid, and sodium alginate was used as the alkali metal salt of an acidic polysaccharide in the binder system. An acrylamide copolymer was used as the binder polymer.

The slurry composition comprised from about 90 to 98 wt% cathode active material, from about 0 to about 3 wt% conductive agent, from about 0.05 to 2 wt% acid or salt thereof, from about 0.1 to 3 wt% alkali metal salt of an acidic polysaccharide and from about 1 to 5 wt% acrylamide copolymer, based on the total weight of the dry composition (i.e. the slurry composition excluding the dispersing medium, or alternatively the electrode).

The peel strength of a cathode prepared with Example 4 is shown in Figure 3.

Comparative Example 1

A cathode was prepared from a slurry composition described herein using the same method as Example 2 and with water as dispersing media, but without any binder (i.e. acrylic) polymer.

The peel strength of a cathode prepared with Comparative Example 1 is shown in Figure 3.

Experimental Example 1

Peel Strength

For the cathodes prepared according to Examples 1 to 4 (water and/or NMP-based) and Comparative Example 1 (without binder/acrylic polymer), the peel strength was measured using the peel strength test according to the method as described herein.

The results are displayed in Figures 3 and 4, which shows that excellent peel strengths are obtained for cathodes prepared from the slurry composition of the disclosure.

Experimental Example 2

pH stability

A slurry composition was prepared according to Example 2 and using water as the dispersing media.

A comparative slurry composition was prepared using a conventional binder system, comprising an acrylic polymer and carboxymethyl cellulose as binder, but without an alkali metal salt of an acidic polysaccharide or an acid.

The pH of the slurry compositions was measured over a period of 0 to 7 days. The results are plotted in Figures 5 and 6. It is clearly visible that the comparative slurry composition without an alkali metal salt of an acidic polysaccharide or acid reaches a pH greater than the limit for Al corrosion (10.5) within 1 day of preparation, whereas the slurry composition of the disclosure has a pH below this limit for up to 6 days after preparation.

Experimental Example 3

Rheology

Slurry compositions were prepared using according to Example 2 using either water (water-based) or NMP (NMP-based) as dispersing media.

The viscosity of the slurry compositions was measured using a standard shear rate sweep test and the results are plotted in Figure 7. There are clear differences in both the low shear and high shear regions, indicating a difference in the rheological behaviour of the slurry compositions. For example, the higher viscosity for the water-based composition in the low shear region compared to the NMP-based composition may indicate a yield stress type behaviour and/or greater stability during storage (for example, due to sedimentation). The lower viscosity for the water-based composition in the high shear region compared to the NMP-based composition may indicate more favourable properties for manufacturing of the cathode (e.g. less force required for screen printing).

Experimental Example 4

Gas Analysis

Cells were prepared using a cathode formed from the slurry compositions according to Example 2 using either water (water-based) or NMP (NMP-based) as dispersing media. Gas analysis is carried out on the cell using online electrochemical mass spectroscopy (OEMS).

The gas evolution (CO_2) from the cells was measured following preparation and up to 40 hours after preparation. The results are plotted in Figure 8.

It is clearly evident that the CO_2 generation is significantly lower for the water-based sample over the 40-hour period, indicating a reduced level of leaching of nickel from the cathode active material.

Experimental Example 3

Capacity Retention

A coin cell was prepared with a similar design to Example 2, but using graphite as the anode. The cell showed 80% capacity retention after 800 cycles.

Unless otherwise indicated, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention pertains.

All embodiments of the invention and particular features mentioned herein may be taken in isolation or in combination with any other embodiments and/or particular features mentioned herein (hence describing more particular embodiments and particular features as disclosed herein) without departing from the disclosure of the invention.

As used herein, the term "comprises" will take its usual meaning in the art, namely indicating that the component includes but is not limited to the relevant features (i.e. including, among other things). As such, the term "comprises" will include references to the component consisting essentially of the relevant substance(s).

Wherever the word 'about' is employed herein in the context of amounts, for example absolute amounts, weights, volumes, sizes, diameters etc., or relative amounts (e.g. percentages) of individual constituents in a composition or a component of a composition (including concentrations and ratios), timeframes, and parameters such as temperatures etc., it will be appreciated that such variables are approximate and as such may vary by ±10%, for example ±5% and preferably ±2% (e.g. ±1%) from the actual numbers specified herein. This is the case even if such numbers are presented as percentages in the first place (for example 'about 10%' may mean ±10% about the number 10, which is anything between 9% and 11%).'

Claims

1. A slurry composition comprising:
a cathode active material;
a binder system;
a dispersing medium; and
optionally a conductive agent,
wherein the binder system comprises:
a binder polymer,
an alkali metal salt of an acidic polysaccharide, and
an acid or salt thereof.

2. The slurry composition according to claim 1, wherein the slurry composition has a solids content of from 60 to 80 wt%.

3. The slurry composition according to claim 1 or claim 2, wherein the binder system is present in an amount of from 1 to 4 wt% of the dry composition.

4. The slurry composition of any preceding claim, wherein the binder polymer is selected from an acrylic polymer, an acrylamide copolymer or mixtures thereof.

5. The slurry composition of any preceding claim, wherein the acrylamide copolymer which is formed from different monomers comprising:
a) 20-80 wt% (meth)acrylamide;
b) 5-50 wt% unsaturated organic acids selected from carboxylic, sulfonic acids, or mixtures thereof, optionally present as alkali metal salts thereof;
c) optionally, 0-75 wt% monomers of hydroxyl group containing vinyl compounds such as hydroxyl containing vinyl ethers.

6. The slurry composition of any preceding claim, wherein the acrylic polymer is selected from one or more of poly(methyl methacrylate), poly(methyl acrylate), poly(ethyl acrylate), poly(butyl acrylate), poly(2-ethylhexyl acrylate), or mixtures thereof.

7. The slurry composition of any preceding claim, wherein the dispersing medium comprises water.

8. The slurry composition of any preceding claim, wherein the acid is selected from one or more of malonic acid, acetic acid, citric acid, polyacrylic acid, alginic acid, phosphoric acid, and mixtures thereof.

9. The slurry composition of any preceding claim, wherein the alkali metal salt of the acidic polysaccharide is a lithium or sodium salt.

10. The slurry composition of any preceding claim, wherein the acidic polysaccharide is alginic acid.

11. The slurry composition of any preceding claim, wherein the cathode active material comprises a lithium nickel manganese cobalt oxide.

12. An electrode formed from the slurry composition of any preceding claim.

13. A method of making a slurry composition comprising the steps of:

a. providing a composition comprising a cathode active material, an acid, an alkali metal salt of an acidic polysaccharide, a binder polymer, optionally a conductive agent, and optionally a dispersing medium; and

b. adding dispersing medium to the composition and mixing to provide a slurry composition having a solids content of from 60 wt% to 80 wt%;

provided that when the binder polymer comprises an acrylic polymer, the method comprises adding said acrylic polymer, optionally together with dispersing medium, to an intermediate slurry composition having solids content of from 65 wt% to 85 wt%, and mixing to provide a slurry composition having a solids content of from 60 wt% to 80 wt%.

14. The method of claim 13, wherein the binder polymer is according to any of claims 4, 5 and/or 6, and/or the dispersing medium is according to claim 7, and/or the acid is according to claim 8, and/or the alkali metal salt of the acidic polysaccharide is according to claim 9 and/or claim 10, and/or wherein the cathode active material is according to claim 11.

15. An electrode comprising:

a cathode active material;
a binder system; and
optionally a conductive agent,
wherein the binder system comprises:

a binder polymer,
an alkali metal salt of an acidic polysaccharide, and
an acid or salt thereof.

16. The electrode of claim 15, wherein the binder polymer is according to any of claims 4, 5 and/or 6, and/or the acid is according to claim 8, and/or the alkali metal salt of the acidic polysaccharide is according to claim 9 and/or claim 10, and/or the cathode active material is according to claim 11.

17. A cell comprising the electrode of claim 15 or claim 16.

18. A battery system comprising the cell according to Claim 17.

19. A vehicle comprising the battery system according to Claim 18.

20. A method of making an electrode comprising
providing a slurry composition according to any one of claims 1 to 11; and
processing the slurry composition to form an electrode.

21. The method of claim 20, wherein the processing comprises
coating a conductive foil with the slurry composition; and
removing the dispersing medium to provide an electrode.

22. A binder system for an electrode comprising:
a binder polymer,
an alkali metal salt of an acidic polysaccharide, and
an acid or salt thereof.

23. The binder system of claim 22, wherein the binder polymer is according to any of claims 4, 5 and/or 6, and/or the acid is according to claim 8, and/or the alkali metal salt of the acidic polysaccharide is according to claim 9 and/or claim 10.

24. The binder system of claim 22 or claim 23, wherein the binder system comprises about 5 to 50 wt% of a binder polymer, about 10 to 60 wt% of an alkali metal salt of an acidic polysaccharide and about 10 to 75 wt% of an acid or salt thereof, based on the weight of the non-volatile content of the binder system.

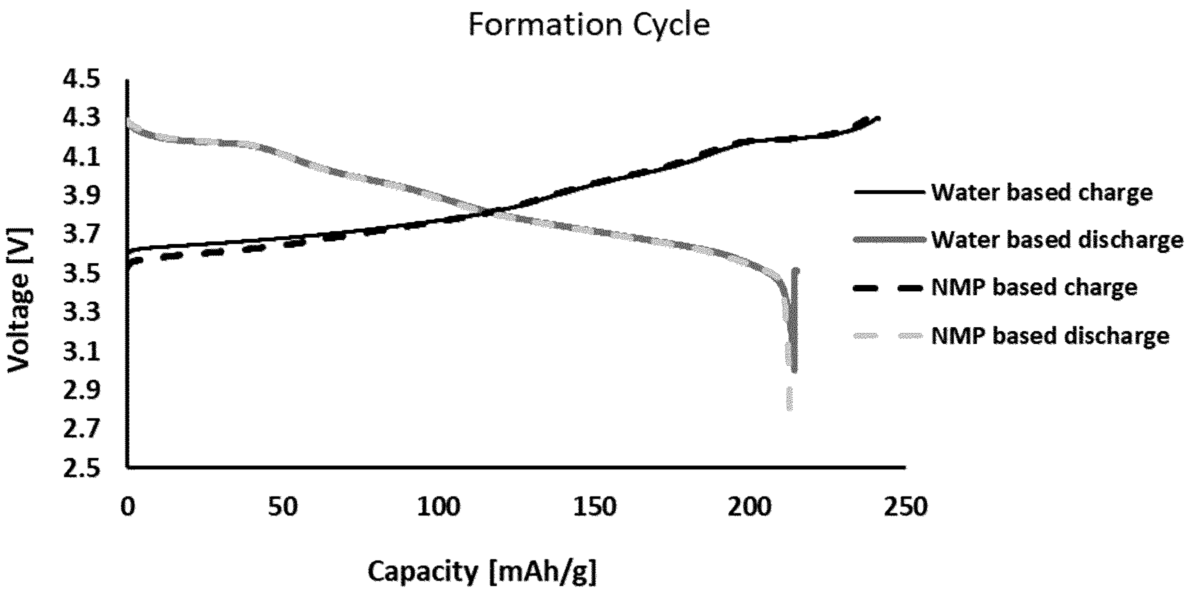

Figure 1

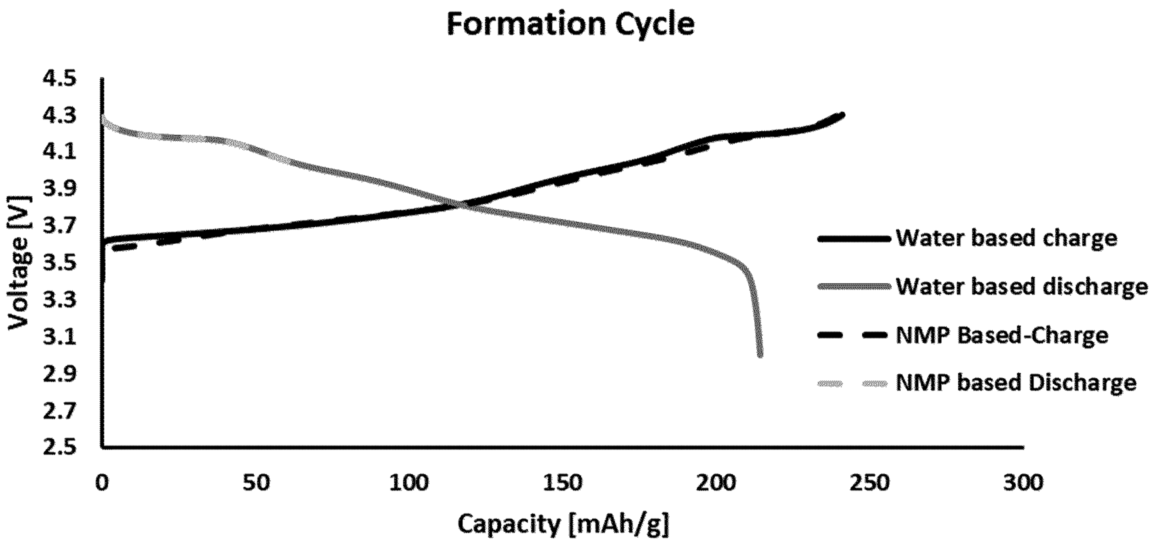

Figure 2

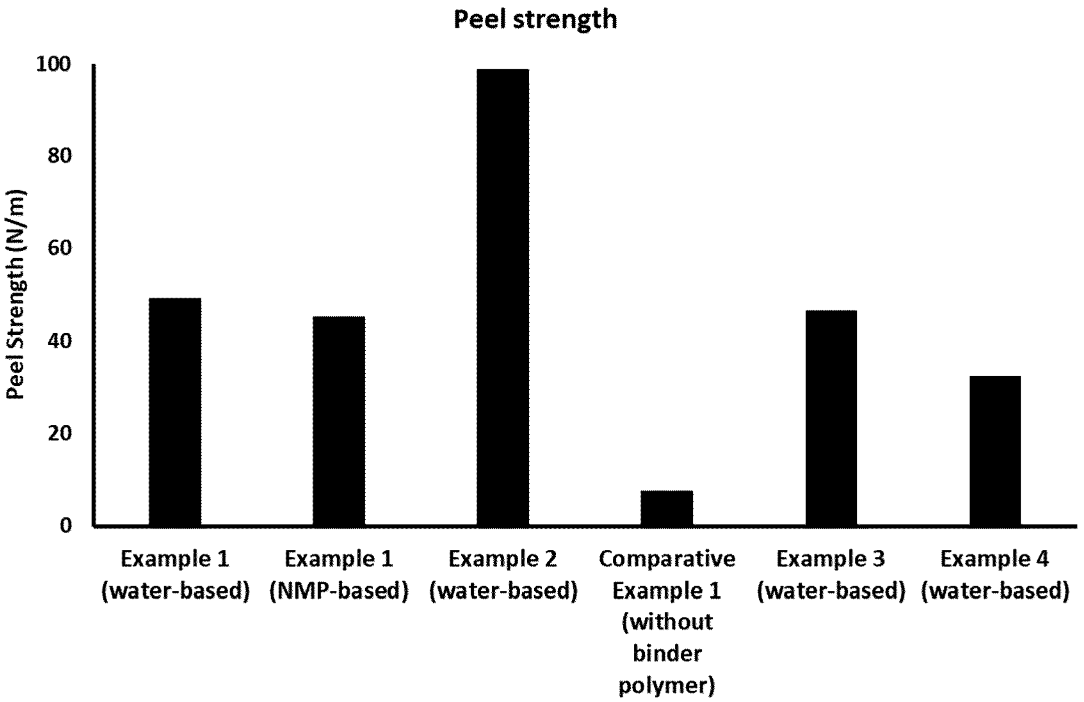

Figure 3

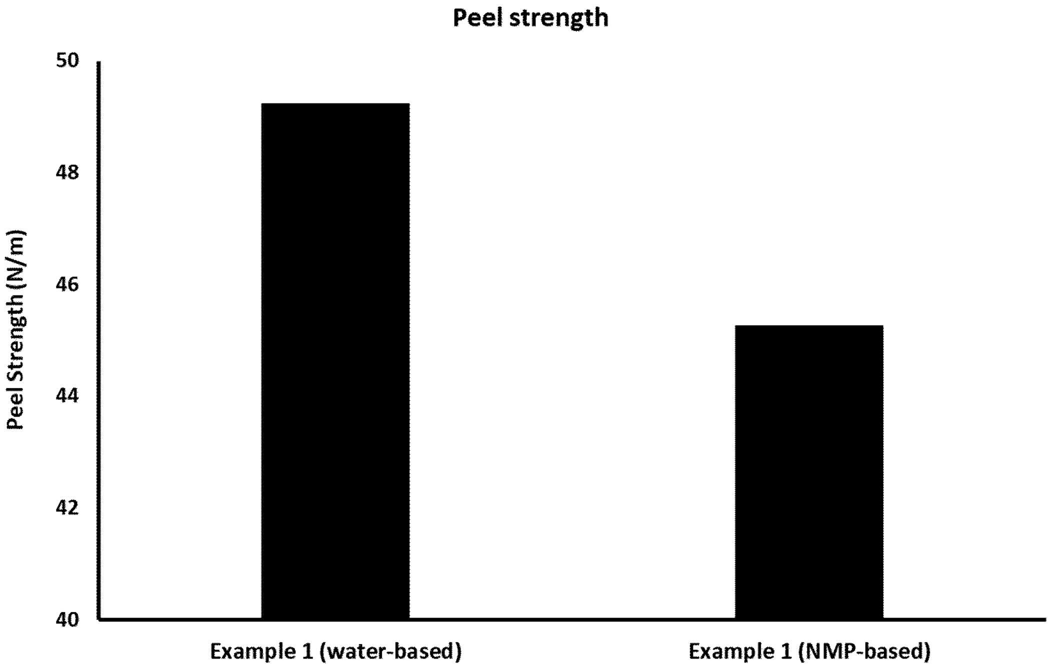

Figure 4

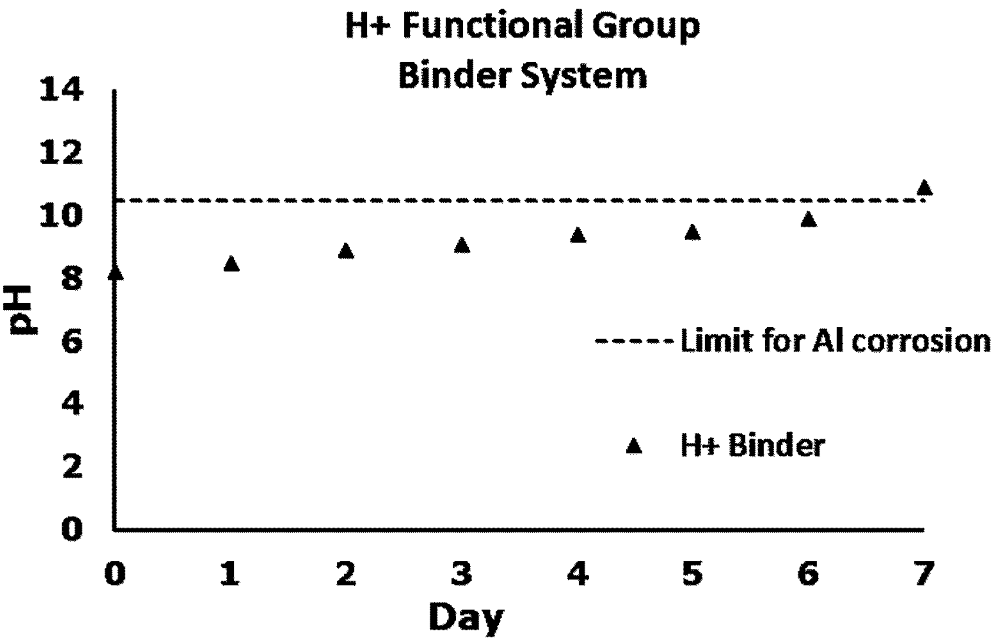

Figure 5

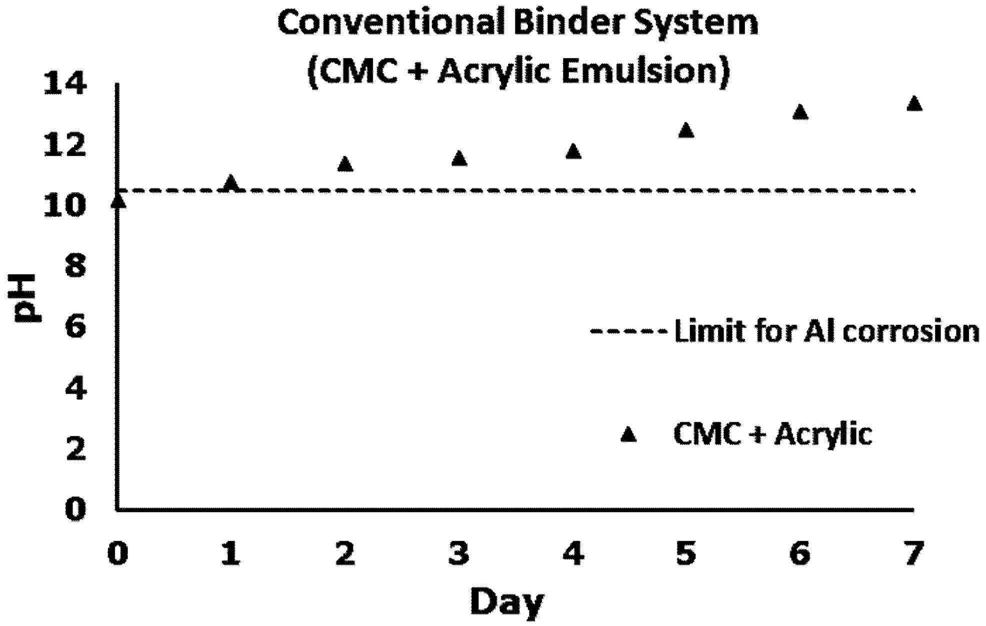

Figure 6

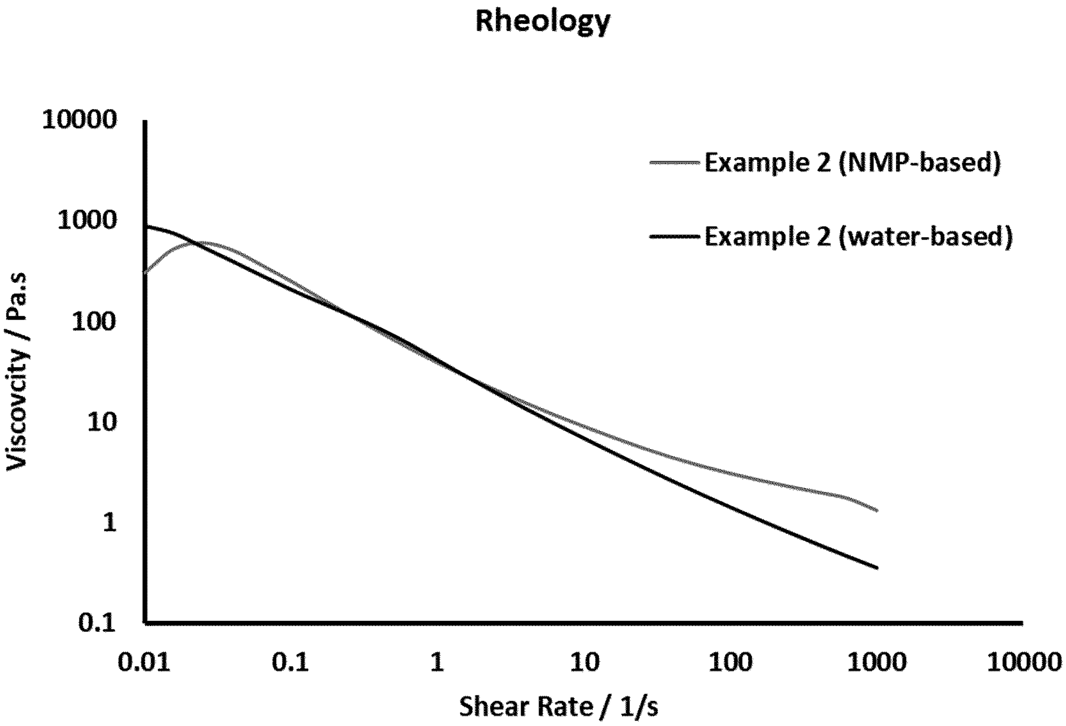

Figure 7

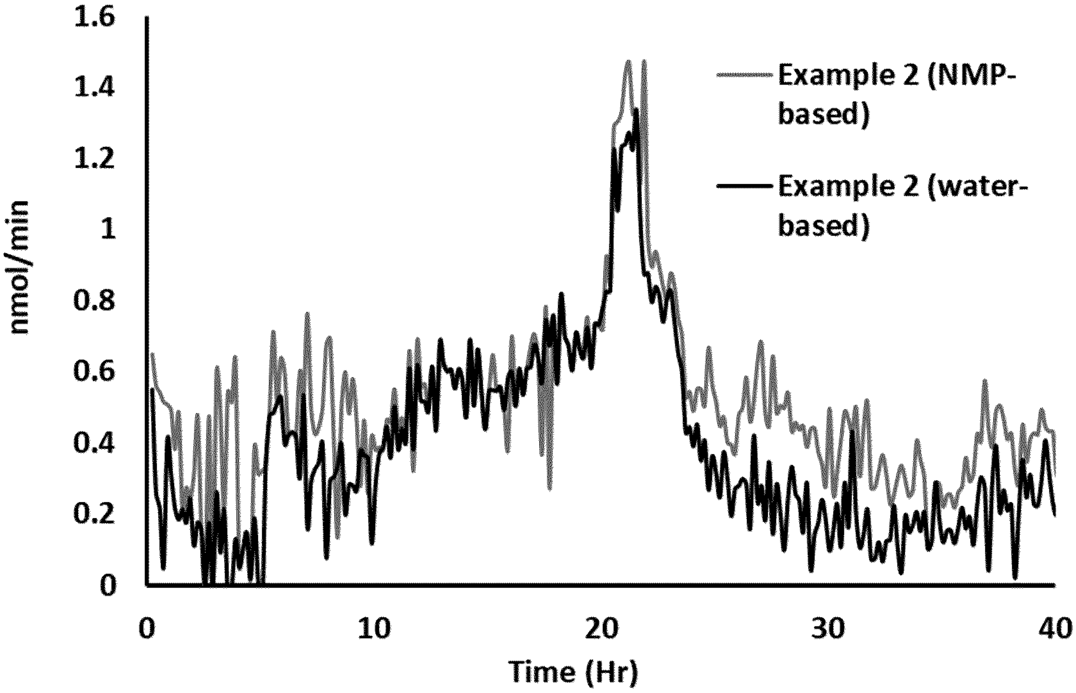

Figure 8

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2023/083862

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M4/50 H01M4/52 H01M4/525 H01M4/60 H01M4/62
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 112 968 177 A (GUANGZHOU GREAT POWER ENERGY & TECH CO LTD) 15 June 2021 (2021-06-15) paragraphs [0081], [0082], [0095] - [0103], [0112], [0113], [0118], [0119]; claims 1-10; example 4; table 1 -----	1-24
A	EP 3 758 116 A1 (ZEON CORP [JP]) 30 December 2020 (2020-12-30) paragraph [0164]; claim 1; example 1 -----	5
A	EP 3 073 555 A2 (AUTOMOTIVE ENERGY SUPPLY CORP [JP]) 28 September 2016 (2016-09-28) paragraphs [0003], [0055] -----	6,19

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 25 April 2024	Date of mailing of the international search report 08/05/2024
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Rausch, Elisabeth

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2023/083862

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