METHOD OF CHARGING AND/OR DISCHARGING A SULFUR BASED BATTERY

Technical Field

The present invention relates, in general terms, to methods of cycling a sulphur based battery. The present invention also relates to methods of charging and/or discharging a sulphur based battery.

Background

Sulfur has a theoretical specific capacity of ~1,675 mAh/$g_{(S)}$, which involves the transfer of 16 electrons per S_8 molecule during an electrochemical reaction. Each electron provides a capacity of ~104.69 mAh/$g_{(S)}$. Many electroactive species are produced during the charge and discharge of lithium-sulfur (Li-S) batteries that use prevailing ether based electrolytes. There are electrolyte soluble species like the Li_2S_8, Li_2S_6, and Li_2S_4 (higher-order polysulfides), and non-soluble species like the Li_2S_2 and Li_2S (lower-order polysulfides).

The complete reaction can be summed up as a 3 phase reaction:

I. Solid-liquid phase reaction ($S_{8(sol.)} \leftrightarrow Li_2S_{8(liq.)} \leftrightarrow Li_2S_{6(liq.)}$), 2 electrons
II. Liquid–solid phase reaction ($Li_2S_{6(liq.)} \leftrightarrow Li_2S_4 \leftrightarrow Li_2S_3 \leftrightarrow Li_2S_{2(sol.)}$), 6 electrons
III. Solid-solid phase reaction ($Li_2S_{2(sol.)} \leftrightarrow Li_2S_{(sol.)}$), 8 electrons

During discharge, the electrochemical reactions causes sulfur to be dissolved in the electrolyte in the form of polysulfides. It is well accepted that 50% of the total theoretical capacity (i.e. 837.5 mAh/$g_{(S)}$), comes from the solid-solid phase reaction (III - conversion of Li_2S_2 to Li_2S). This redox reaction is kinetically slower compared to the previous two phase reactions (I and II). Also, the formation of Li_2S on the electrode could lead to irreversible capacity loss and an increase in cell impedance. Li_2S forms/deposits on the anode promoting the polysulfide shuttling (PS), which lower the Coulumbic efficiency, causes overcharging and cell degradation. On the cathode, during charging, the Li_2S conversion to Li_2S_2 is kinetically not favourable, for example, at high current rate operations (lower electrical and ionic conductivities, etc.).

To avoid Li_2S formation, the Li-S battery can be operated in the phases where only the higher-order polysulfides are formed (phase reactions I and II), which can reduce the risk of polysulfide shuttling but would restrict the capacity to only 50% of the theoretical value (837.5 $mAh/g_{(S)}$, assuming 100% sulfur utilization). There are various techniques employing cathode, separator, and electrolyte modifications proposed to avoid polysulfide shuttling. However, none of them till-date has successfully improved the cycle life performance of Li-S cell to reach commercial standards. The commercial Li-S battery only offers a cycle life between 60-100 cycles.

It would be desirable to overcome or ameliorate at least one of the above-described problems.

Summary

The present disclosure provides a method to operate an alkali and alkaline-earth metals/alloys-sulfur batteries. The method does not rely on the battery cell configuration, for example modifications to the cathode, anode, separator, and/or electrolyte. The method can improve the cycle life and prevent the overcharging of the batteries by the controlling the formation of intermediary polysulfide species using the specific capacities and voltages as the limiting factors to charge/discharge the cells.

The present invention provides a method of charging and/or discharging a sulphur based battery, comprising:

a) limiting a charge and/or discharge specific capacity of the battery based on

$$specific\ capacity\ (limit) = total\ specific\ capacity \times \frac{n}{16}$$

wherein the total specific capacity is the specific capacity of the battery derived from complete charging and/or discharging; and

n is a number of electrons transferred in redox reactions between sulphur and/or its chemical species thereof; and

b) limiting a charge and/or discharge voltage of the battery based on a rate of change of voltage relative to an electric parameter of the battery, in which the rate of change represents a transition between redox reactions of sulphur and/or its chemical species thereof.

Disclosed herein is a method of charging and/or discharging a sulphur-based battery,

comprising:

a) limiting a charge and/or discharge specific capacity of the battery based on

$$specific\ capacity\ (limit) = practical\ specific\ capacity \times \frac{n}{16}$$

wherein the practical specific capacity is the specific capacity of the battery derived from complete charging and/or discharging; and

n is a number of electrons transferred in redox reactions between sulphur and/or its chemical species thereof; and

b) limiting a charge and/or discharge voltage of the battery based on a rate of change of voltage relative to an electric parameter of the battery, in which the rate of change represents a transition between redox reactions of sulphur and/or its chemical species thereof;

wherein the limit of the charge and/or discharge specific capacity of the battery is adjustable in a stepwise manner based on the number of electrons transferred in redox reactions between sulphur and/or its chemical species thereof; and

wherein the limit of the charge and/or discharge voltage of the battery is adjustable in a stepwise manner based on the type of redox reactions between sulphur and/or its chemical species thereof.

Early works involves under-charging or under-discharging the battery in order to prolong battery life. This is usually done by keeping batteries at a state of charge (SoC) fixed at 85-25% i.e. charge till 85% and discharge (DoD) till 25%. This approach increases cycle life to 2000 cycles but gives only 60% rated energy density. Such an approach works easily in a battery system controlled by intercalation chemistries but not in conversion chemistries like Li-S or Silicon anode based batteries. In contrast, the present disclosure provides a method where the charge and/or discharge of a battery is terminated using both capacity and voltage as the limit calculated using a protocol as disclosed herein. The protocol calculates the limit during real-time operation of the battery using the galvanic charge-discharge characteristic of the battery. This method may be incorporated into the battery management system (BMS) of the battery pack to constantly monitor the battery and control it during operation. Incorporation of this method within the BMS provides certain level of intelligence to it thereby allowing the manufacturer to extend the cycle-life or life-time of the battery pack by improving its state of health (SoH).

In some embodiments, the limit of the charge and/or discharge specific capacity of the battery is adjustable in a stepwise manner based on the number of electrons transferred in redox reactions between sulphur and/or its chemical species thereof.

In some embodiments, the limit of the charge and/or discharge specific capacity of the battery is adjustable in real time during operation of the battery.

In some embodiments, the total specific capacity is derived from a theoretical specific capacity for sulphur which is 1675 mAh/$g_{(S)}$.

In some embodiments, n is an even number.

In some embodiments, when the total specific capacity is about 1,675 mAh/g(S), each electron transfer is characterised by a specific capacity of about 104 mAh/$g_{(S)}$.

In some embodiments, the specific capacity is limited based on 2, 4, 5, 6, 7, 8, 9, 10, 12, 14 or 15 electrons redox reaction between sulphur and/or its chemical species thereof.

In some embodiments, the method further comprises capping a lower limit of the charge and/or discharge specific capacity to a percentage of the specific capacity (limit).

In some embodiments, the 6 electron redox reaction between sulphur and/or its chemical species thereof is selected from:

$$S_6^{2-}{}_{(\sim 75\%)} \leftrightarrow S_4^{2-} \leftrightarrow S_3^{2-} \leftrightarrow S_2^{2-} \leftrightarrow S^{2-}{}_{(\sim 35\%)}$$

$$S_8 \leftrightarrow S_8^{2-} \leftrightarrow S_6^{2-} \leftrightarrow S_4^{2-}$$

.

In some embodiments, when the battery is limited to a 6 electron redox reaction, the specific capacity is limited to about 628 mAh/$g_{(S)}$.

In some embodiments, the 8 electron redox reaction between sulphur and/or its chemical species thereof is selected from:

$$S_6^{2-} \leftrightarrow S_4^{2-} \leftrightarrow S_3^{2-} \leftrightarrow S_2^{2-} \leftrightarrow S^{2-}{}_{(\sim 35\%)}$$

$$S_8 \leftrightarrow S_8^{2-} \leftrightarrow S_6^{2-} \leftrightarrow S_4^{2-} \leftrightarrow S_{2\text{-}3}^{2-}$$

.

In some embodiments, when the battery is limited to a 8 electron redox reaction, the specific capacity is limited to about 837.5 mAh/$g_{(S)}$.

In some embodiments, the 10 electron redox reaction between sulphur and/or its chemical species thereof is selected from:

$$S_{8(60\%)} \leftrightarrow S_8^{2-} \leftrightarrow S_6^{2-} \leftrightarrow S_4^{2-} \leftrightarrow S_3^{2-} \leftrightarrow S_2^{2-} \leftrightarrow S^{2-}{}_{(35\%)}$$

.

In some embodiments, when the battery is limited to a 10 electron redox reaction, the specific capacity is limited to about 1,046.9 mAh/$g_{(S)}$.

In some embodiments, the 12 electron redox reaction between sulphur and/or its chemical species thereof is selected from:

$$S_8 \leftrightarrow S_8^{2-} \leftrightarrow S_6^{2-} \leftrightarrow S_4^{2-} \leftrightarrow S_3^{2-} \leftrightarrow S_2^{2-} \leftrightarrow S^{2-}{}_{(50\%)}$$

.

In some embodiments, when the battery is limited to a 12 electron redox reaction, the specific capacity is limited to about 1,256.25 mAh/$g_{(S)}$.

In some embodiments, the limit of the charge and/or discharge voltage of the battery is adjustable in a stepwise manner based on the type of redox reactions between sulphur and/or its chemical species thereof.

In some embodiments, the limit of the charge and/or discharge voltage of the battery is adjustable in real time during operation of the battery.

In some embodiments, the voltage is limited based on a rate of change of charge relative to voltage.

In some embodiments, the rate of change of charge relative to voltage is a first order derivative of a current-voltage function.

In some embodiments, the voltage is limited based on a negative peak in a first order derivative of a current-voltage function.

In some embodiments, the current-voltage function is obtained from a cyclic voltammetry measurement.

In some embodiments, the rate of change of charge relative to voltage is a second order derivative of a capacity-voltage function.

In some embodiments, the voltage is limited based on a negative peak in a second order derivative of a capacity-voltage function.

In some embodiments, the voltage is limited based on an intersect of extrapolated tangents at a deflection point or inflection point of a capacity-voltage function.

In some embodiments, the capacity-voltage function is obtained from a galvanic charge (GChg) plot.

In some embodiments, when the battery is limited to a 6 electron redox reaction, the charge voltage is limited to about 2.3 V to about 2.5 V.

In some embodiments, when the battery is limited to a 6 electron redox reaction, the charge voltage is limited to about 2.33 V or about 2.42 V.

In some embodiments, when the battery is limited to a 8 electron redox reaction, the charge voltage is limited to about 2.3 V to about 2.4 V.

In some embodiments, when the battery is limited to a 8 electron redox reaction, the charge voltage is limited to about 2.33 V or about 2.37 V.

In some embodiments, when the battery is limited to a 10 electron redox reaction, the charge voltage is limited to about 2.3 V to about 2.4 V.

In some embodiments, when the battery is limited to a 10 electron redox reaction, the charge voltage is limited to about 2.37 V.

In some embodiments, the sulphur based battery is an alkali metal-sulfur battery, alkaline-earth metal-sulfur battery, alloy-sulfur battery, or a metal-sulfur battery wherein the metal is selected from aluminium, vanadium, titanium, molybdenum, iron, niobium, or tungsten.

In some embodiments, the alkali metal is selected from Li, Na, K, or a combination thereof.

In some embodiments, the alkaline-earth metal is selected from Mg, Ca, Sr, Ba, or a combination thereof.

In some embodiments, the alloy is selected from Li-Sn, Li-Mg, Li-B, Li-Si, Li-Hg, Li-Al, sodium alloy, aluminium alloy, potassium alloy and magnesium alloy.

The present invention also provides a battery management system, wherein the battery management system is configured to:

a) limit a charge and/or discharge specific capacity of the battery based on

$$specific\ capacity\ (limit) = total\ specific\ capacity \times \frac{n}{16}$$

wherein the total specific capacity is the specific capacity of the battery derived from complete charging and/or discharging; and

n is a number of electrons transferred in redox reactions between sulphur and/or its chemical species thereof; and

b) limit a charge and/or discharge voltage of the battery based on a rate of change of voltage relative to an electric parameter of the battery, in which the rate of change represents a transition between redox reactions of sulphur and/or its chemical species thereof.

Disclosed herein is a battery management system, wherein the battery management system is configured to:

a) limit a charge and/or discharge specific capacity of the battery based on

$$specific\ capacity\ (limit) = practical\ specific\ capacity \times \frac{n}{16}$$

wherein the practical specific capacity is the specific capacity of the battery derived from complete charging and/or discharging; and

n is a number of electrons transferred in redox reactions between sulphur and/or its chemical species thereof; and

b) limit a charge and/or discharge voltage of the battery based on a rate of change of voltage relative to an electric parameter of the battery, in which the rate of change represents a transition between redox reactions of sulphur and/or its chemical species thereof;

wherein the limit of the charge and/or discharge specific capacity of the battery is adjustable in a stepwise manner based on the number of electrons transferred in redox reactions between sulphur and/or its chemical species thereof; and

wherein the limit of the charge and/or discharge voltage of the battery is adjustable in a stepwise manner based on the type of redox reactions between sulphur and/or its chemical species thereof.

In some embodiments, the limit of the charge and/or discharge specific capacity of the battery is adjustable in a stepwise manner based on the number of electrons transferred in redox reactions between sulphur and/or its chemical species thereof.

In some embodiments, the limit of the charge and/or discharge voltage of the battery is adjustable in a stepwise manner based on the type of redox reactions between sulphur and/or its chemical species thereof.

In some embodiments, the limit to the specific capacity and/or voltage is adjustable by a control means.

In some embodiments, the limit to the specific capacity and/or voltage is adjustable by a user.

Brief description of the drawings

Embodiments of the present invention will now be described, by way of non-limiting example, with reference to the drawings in which:

Figure 1 shows a first specific discharge capacity for a Li-S cell at 0.05 C-rate.

Figure 2 shows an example of method to determine the charging voltage limits by second order derivative of capacity as a function of voltage obtained from the galvanic charge tests.

Figure 3 shows an example of determination of voltage limits by extrapolated tangents method using data from the voltage as a function of charge capacity obtained from the galvanic charge tests.
Figure 4 shows capacity retention vs. cycle life plot for a Li-S cell tested at 0.2 current rate with discharge voltage limit of 1.8 V for 10-, 8-, 6-electron protocol and standard protocol.

Detailed description

It should be noted that while the embodiments relate to Li-S batteries, the invention is not limited to as such. The methods can also be applied to all types of alkali and alkaline-earth metal/alloy-sulfur batteries and may be used in any possible combinations.

The present invention is based on the understanding that a Li-S battery can be operated between 1.0 V and 3.0 V. Typically, during the operation of a Li-S battery, the battery is discharged and charged at a constant-current until cut-off voltages between 1.0 V and 2.0 V, and 2.2 V and 3.0 V, respectively. During the discharge process (example at Figure 1), sulfur (S_8) is reduced first to high-order polysulfides Li_2S_x ($8 \geq x \geq 4$) and then to low-order polysulfides Li_2S_x ($4 > x \geq 1$). Among the most challenging issues in electrochemical energy storage is controlling the species formed while cycling cells that operate on the basis of chemical transformations, like the redox processes of Li-S batteries.

In Li-S batteries, dissolution of the metallic lithium occurs at the anode, with the production of electrons and lithium ions during the discharge:

$$Li \rightarrow Li^+ + e^-$$

During the discharge, the lithium ions in the electrolyte migrate to the cathode where the sulfur is reduced to lithium sulphide (Li_2S). The sulfur is reoxidized to S_8 during the refilling phase. This involves the formation of lithium polysulphides (Li_2Sx, $2 \leq x \leq 8$) at decreasing chain length according to:

$$S_8 \rightarrow Li_2S_8 \rightarrow Li_2S_6 \rightarrow Li_2S_4 \rightarrow Li_2S_3 \rightarrow Li_2S_2 \rightarrow Li_2S$$

In Li–S batteries using ether-based organic electrolyte, there are two main discharge plateaus, one at ~2.3 and another at ~2.1 V, which correspond to the transformations

of S_8 to Li_2S_4 and Li_2S_4 to Li_2S, respectively, with the intermediate products of S_8^{2-}, S_6^{2-}, S_4^{2-}, and $S_3^{\bullet-}$. During the following charge process, Li_2S is oxidized to elemental sulfur (S_8) via the formation of the same intermediate lithium polysulfides. The chemical transformations during charge and discharge coincide with the voltage rise and fall observed in the capacity as a function of voltage plots.

The present invention provides a method of charging and/or discharging a sulphur based battery, comprising:

a) limiting a charge and/or discharge specific capacity of the battery based on

$$specific\ capacity\ (limit) = total\ specific\ capacity \times \frac{n}{16}$$

wherein the total specific capacity is the specific capacity of the battery derived from complete charging and/or discharging; and

n is a number of electrons transferred in redox reactions between sulphur and/or its chemical species thereof; and

b) limiting a charge and/or discharge voltage of the battery based on a rate of change of voltage relative to an electric parameter of the battery, in which the rate of change represents a transition between redox reactions of sulphur and/or its chemical species thereof.

One of the shortfalls of Li–S cells is unwanted or undesirable reactions with the electrolytes. While S and Li_2S are relatively insoluble in most electrolytes, many intermediate polysulfides are not. Dissolving Li_2S_n into electrolytes causes irreversible loss of active sulfur. For example, lithium polysulfide Li_2S_x ($6 \leq x \leq 8$) is highly soluble in common electrolytes used for Li–S batteries. They can be formed and leaked from the cathode and they diffuse to the anode, where they are reduced to short-chain polysulfides and diffuse back to the cathode where long-chain polysulfides are formed again. This process results in the continuous leakage of active material from the cathode, lithium corrosion, low coulombic efficiency and low battery life. Moreover, the "shuttle" effect is responsible for the characteristic self-discharge of Li–S batteries, because of slow dissolution of polysulfide, which occurs also in rest state.

In contrast to early works which under-charge or under-discharge the battery in order to reduce the rate of capacity fade and hence prolong the battery life, the present disclosure improves the cycle life of the battery by calculating the limit during real-time operation of the battery using the galvanic charge-discharge characteristic of the

battery. The battery is also prevented from overcharging which thus slows down the degradation of the battery. This is achieved by limiting the capacity and voltage to certain set of redox reactions. These redox reactions have a well defined count of electrons that are used during charge or given during discharge. By operating the battery based on the number of electrons, the redox reactions occurring in the battery can be controlled. As the electron count in the redox reactions is constant, the pattern is always the same.

Redox reactions occur at certain specific voltages or commonly called as 'standard redox potential' and charge controls the number of said redox species being transformed at that specific voltage. Charge can be performed initially under a 'constant current' followed by a 'constant voltage', where the constant voltage is the voltage limit value as provided in this invention for a pre-defined operation. The charge can also be directly peformed in a CCCV mode or 'constant current and constant voltage mode'. Discharge is performed in a constant current mode. Each of them has specific relevance in the operation of the battery as it will determine how much of the said species is fully transformed; i.e. the required number or redox species as set by the method that can be obtained.

A battery is a device that converts chemical energy into electrical energy and vice versa. A cell is the smallest, packaged form a battery can take and is generally on the order of one to six volts. A module consists of several cells generally connected in either series or parallel. A battery pack can then be assembled by connecting modules together, again either in series or parallel. As used herein, the cell, module and battery pack are within the scope of a battery. Also included within the scope is secondary batteries, in which a secondary battery is one that is rechargeable.

The cell typically includes an anode, a cathode, an electrolyte and, preferably, a porous separator, which may advantageously be positioned between the anode and the cathode. The anode may be formed of alkali metal, alkali-earth or a metal alloy. Preferably, the anode is a metal foil electrode, such as a lithium foil electrode. The lithium foil may be formed of lithium metal or lithium metal alloy. The cathode of the cell can include a mixture of electroactive sulphur material and electroconductive material. This mixture forms an electroactive layer, which may be placed in contact with a current collector. The mixture of electroactive sulphur material and electroconductive

material may be applied to the current collector in the form of a slurry in a solvent (e.g. water or an organic solvent). The solvent may then be removed and the resulting structure calendared to form a composite structure, which may be cut into the desired shape to form a cathode. A separator may be placed on the cathode and a lithium anode placed on the separator. Electrolyte may then be introduced into the assembled cell to wet the cathode and separator.

The electroactive sulfur material relates to cathode active materials which comprise the element sulfur in any form, wherein the electrochemical activity involves the breaking or forming of sulfur-sulfur covalent bonds. Examples of suitable electroactive sulfur-containing materials include, but are not limited to, elemental sulfur and organic materials comprising both sulfur atoms and carbon atoms, which may or may not be polymeric. Suitable organic materials include those further comprising heteroatoms, conductive polymer segments, composites, and conductive polymers. In one embodiment, the electroactive sulfur-containing material comprises elemental sulfur. In another embodiment, the electroactive sulfur-containing material comprises a mixture of elemental sulfur and a sulfur-containing polymer.

The cathode may further comprise electroactive metal chalcogenides, electroactive conductive polymers, and combinations thereof. The cathode may further comprise one or more conductive fillers to provide enhanced electronic conductivity. The cathode may also comprise a binder. The choice of binder material may vary widely. Useful binders are those materials, usually polymeric, that allow for ease of processing of battery electrode composites and are known to those skilled in the art of electrode fabrication. The cathode may further comprise one or more N—O additive of the present invention.

The organic solvent used in the electrolyte should be capable of dissolving the polysulphide species, for example, of the formula S_n^{2-}, where n = 2 to 12, that are formed when the electroactive sulphur material is reduced during discharge of the cell. Suitable organic solvents are tetrahydrofurane, 2-methyltetrahydrofurane, dimethylcarbonate, diethylcarbonate, ethylmethylcarbonate, methylpropylcarbonate, methylpropylpropionate, ethylpropylpropionate, methyl acetate, dimethoxyethane, 1, 3-dioxolane, diglyme (2-methoxyethyl ether), tetraglyme, ethylene carbonate, propylene carbonate, γ-butyrolactone, dioxolane, hexamethyl phosphoamide, pyridine, dimethyl sulfoxide, tributyl phosphate, trimethyl phosphate, and sulfone and their

mixtures. Preferably, the organic solvent is a sulfone or a mixture of sulfones. Examples of sulfones are dimethyl sulfone and sulfolane. Sulfolane may be employed as the sole solvent or in combination, for example, with other sulfones.

Capacity of a battery refers to how much energy the battery can hold (in Ah or Wh). The specific-capacity refers to how much energy the battery can hold per unit weight (for example, in Ah/g or Wh/g).

The specific capacity defines the amount of electric charge (Ah) the material can deliver per kilogram of active battery material. The discharge specific capacity refers to the specific capacity the material can deliver when a load is applied to the battery till the voltage reaches the lower cut-off voltage, as determined by the redox limits of the active battery materials or specified by the operational control system, being the last higher or equal to the redox limits of the materials.

The charge specific capacity refers to the specific capacity the material can deliver when a charge potential is applied to the battery till the voltage reaches the upper cut-off voltage, as determined by the redox limits of the active battery materials or specified by the operational control system, being the last always lower or equal to the redox limits of the materials.

Voltage of a battery is determined by the chemical reactions in the battery, the concentrations of the battery components, and the polarization of the battery. The voltage calculated from equilibrium conditions is typically known as the nominal battery voltage. In practice, the nominal battery voltage cannot be readily measured, but for practical battery systems (in which the overvoltages and non-ideal effects are low) the open circuit voltage is a good approximation to the nominal battery voltage.

The charge and/or discharge voltage refers to the voltage that the battery is charged/discharged to when charged/discharged to full/zero capacity. Charging schemes generally consist of a constant current charging until the battery voltage reaching the charge voltage, then constant voltage charging, allowing the charge current to taper until it is very small.

In some embodiments, the specific capacity is limited based on

$$specific\ capacity\ (limit) = \frac{total\ specific\ capacity}{16} \times n$$

wherein the total specific capacity is the specific capacity of the battery derived from complete charging and/or discharging; and
n is the number of electrons transferred in redox reactions between sulphur and/or its chemical species thereof.

In some embodiments, the limit of the charge and/or discharge specific capacity of the battery is adjustable. In some embodiments, the limit of the charge and/or discharge specific capacity of the battery is adjustable in a stepwise manner based on the number of electrons transferred in redox reactions between sulphur and/or its chemical species thereof. This may be calculated on the battery's charge and/or discharge cycle. Each redox reaction occur at a specific redox potential for that species which is being transformed. Accordingly, when the number of electrons limited is larger than the number of electrons transferred in any of the redox reactions, multiple redox potentials and multiple redox species can be formed/transformed during the charge discharge.

In some embodiments, the limit of the charge and/or discharge specific capacity of the battery is adjustable in real time during operation of the battery. While there might be a slight shift in the redox peaks/potential based on the cell/electrode composition and configuration or pH of the electrolyte, this is not expected to be an issue because the redox peaks will be calculated real-time and further limits are automatically calculated to operate the battery.

In some embodiments, n is an integer from 1 to 16. In some embodiments, n is an integer from 2 to 15. In some embodiments, n is an even number. The even number can be selected from 4, 6, 8, 10, 12 or 14. In some embodiments, n is an odd number, being selected from 3, 5, 7, 9, 11, 13 or 15.

In some embodiments, each electron transfer is characterised by a specific capacity of about 90 mAh/$g_{(S)}$ to about 130 mAh/$g_{(S)}$. In some embodiments, each electron transfer is characterised by a specific capacity of about 104 mAh/$g_{(S)}$. In this regard, the complete electrochemical charge/discharge reactions as a 16 electron reactions deliver about 1,675 mAh/g(S). In some embodiments, the total specific capacity is derived from a theoretical specific capacity for sulphur. In other embodiments, the total specific capacity is 1675 mAh/$g_{(S)}$.

It should be noted that various factors like electrode engineering and composition, cell architecture, and electrolyte can influence the impedance of the cell and thereby the total specific capacity of a given practical cell can vary between a capacity of 200 $mAh/g_{(S)}$ to 1675 $mAh/g_{(S)}$. This will change the range of the "specific capacity limit values" for each 'n' electron reaction. For example, if the total specific capacity of a practical cell is 500mAh/g then the specific capacity limit for 8 electrons will be 250mAh/g.

In some embodiments, the total specific capacity is derived from an initial charge capacity of the battery in a voltage range of 1V to 3V. The initial charge capacity can be measured using a C-rate of 0.01C, 0.02C, 0.05C or 0.1C. Initial charge capacity is obtainable after performing an initial discharge on a freshly fabricated cell within a voltage range of 1V to 3V.

The specific capacity is limited to any number of electrons below 16. In some embodiments, the specific capacity is limited based on 2, 4, 5, 6, 7, 8, 9, 10, 12, 14 or 15 electrons redox reaction between sulphur and/or its chemical species thereof. In some embodiments, the specific capacity is limited based on 6, 8, 10, or 12 electrons redox reaction between sulphur and/or its chemical species thereof. In some embodiments, the specific capacity is limited based on 6, 8, or 10 electrons redox reaction between sulphur and/or its chemical species thereof. In some embodiments, the specific capacity is limited based on 6, 8, 10, 12, 14 or 16 electrons redox reaction between sulphur and/or its chemical species thereof.

In some embodiments, the charge and/or discharge specific capacity of the battery is further limited based on

$$specific\ capacity\ (percent\ limit) = total\ specific\ capacity \times \frac{n}{16} \times (1 - \frac{n}{16})$$

wherein n is a number less than 9.

This advantageously further limits the specific capacity to a percentage of the limited specific capacity.

In some embodiments, the 6 electron redox reaction between sulphur and/or its chemical species thereof is selected from:

$$S_6^{2-}{}_{(\sim 75\%)} \leftrightarrow S_4^{2-} \leftrightarrow S_3^{2-} \leftrightarrow S_2^{2-} \leftrightarrow S^{2-}{}_{(\sim 35\%)}$$

$$S_8 \leftrightarrow S_8^{2-} \leftrightarrow S_6^{2-} \leftrightarrow S_4^{2-}$$

.

The percentages indicated are related to their electron contribution, which represents the amount of species undergoing redox conversion thereby producing the said number of electrons. The remaining amount stay as un-reactive species.

The theoretical limit for 6 electrons i.e. 1675 $\mathrm{X}\left(\frac{6}{16}\right)$ = 628.125 $\mathrm{mAh/g(s)}$ as per the above equation. The theoretical capacity of sulfur is 1675 mAh g^{-1} calculated from standard by Faraday's law: $Q_{theoretical}$ = (nF) / (3600*Mw) mAh g^{-1}.

The lower limit of the specific capacity can be varied based on specific capacity (percent limit) as disclosed above. For example, when n = 6, the specific capacity is 392.58 $mAh/g_{(S)}$, which is about 62.5% of 628.12 $mAh/g_{(S)}$ based on a 6 electron redox reaction. This may be determined depending on the requirements of the applications and desired battery capacity and/or cycle life.

The choice of number of electrons involved in the electron protocol may be any integer number between 2 and 15 and may be determined based on desired battery capacity and cycle life of the battery. This may be dependent on the operational requirements. The electron protocol may be used to deliver more capacity or more cycle life.

In some embodiments, when the battery is limited to a 6 electron redox reaction, the specific capacity is limited to about 390 $mAh/g_{(S)}$ to about 785 $mAh/g_{(S)}$. In other embodiments, the specific capacity is limited to about 400 $mAh/g_{(S)}$ to about 785 $mAh/g_{(S)}$, about 420 $mAh/g_{(S)}$ to about 785$mAh/g_{(S)}$, about 440 $mAh/g_{(S)}$ to about 785$mAh/g_{(S)}$, about 460 $mAh/g_{(S)}$ to about 785$mAh/g_{(S)}$, about 480 $mAh/g_{(S)}$ to about 785$mAh/g_{(S)}$, about 500 $mAh/g_{(S)}$ to about 785$mAh/g_{(S)}$, about 520 $mAh/g_{(S)}$ to about 785$mAh/g_{(S)}$, about 540 $mAh/g_{(S)}$ to about 785$mAh/g_{(S)}$, about 560 $mAh/g_{(S)}$ to about 785$mAh/g_{(S)}$, about 580 $mAh/g_{(S)}$ to about 785$mAh/g_{(S)}$, about 600 $mAh/g_{(S)}$ to about 785$mAh/g_{(S)}$, about 620 $mAh/g_{(S)}$ to about 785$mAh/g_{(S)}$, about 640 $mAh/g_{(S)}$ to about 785$mAh/g_{(S)}$, about 660 $mAh/g_{(S)}$ to about 785$mAh/g_{(S)}$, about 680 $mAh/g_{(S)}$ to about 785$mAh/g_{(S)}$, about 700 $mAh/g_{(S)}$ to about 785$mAh/g_{(S)}$, or about 720 $mAh/g_{(S)}$ to about

785mAh/$g_{(S)}$. In some embodiments, the specific capacity is limited to about 628 mAh/$g_{(S)}$.

In some embodiments, the 8 electron redox reaction between sulphur and/or its chemical species thereof is selected from:

$$S_6^{2-} \leftrightarrow S_4^{2-} \leftrightarrow S_3^{2-} \leftrightarrow S_2^{2-} \leftrightarrow S^{2-}_{(\sim 35\%)}$$

$$S_8 \leftrightarrow S_8^{2-} \leftrightarrow S_6^{2-} \leftrightarrow S_4^{2-} \leftrightarrow S_{2\text{-}3}^{2-}$$

.

In some embodiments, when the battery is limited to a 8 electron redox reaction, the specific capacity is limited to about 410 mAh/$g_{(S)}$ to about 1050 mAh/$g_{(S)}$. In other embodiments, the specific capacity is limited to about 420 mAh/$g_{(S)}$ to about 1050 mAh/$g_{(S)}$, about 440 mAh/$g_{(S)}$ to about 1050 mAh/$g_{(S)}$, about 460 mAh/$g_{(S)}$ to about 1050 mAh/$g_{(S)}$, about 480 mAh/$g_{(S)}$ to about 1050 mAh/$g_{(S)}$, about 500 mAh/$g_{(S)}$ to about 1050 mAh/$g_{(S)}$, about 520 mAh/$g_{(S)}$ to about 1050 mAh/$g_{(S)}$, about 540 mAh/$g_{(S)}$ to about 1050 mAh/$g_{(S)}$, about 560 mAh/$g_{(S)}$ to about 1050 mAh/$g_{(S)}$, about 580 mAh/$g_{(S)}$ to about 1050 mAh/$g_{(S)}$, about 600 mAh/$g_{(S)}$ to about 1050 mAh/$g_{(S)}$, about 620 mAh/$g_{(S)}$ to about 1050 mAh/$g_{(S)}$, about 640 mAh/$g_{(S)}$ to about 1050 mAh/$g_{(S)}$, about 660 mAh/$g_{(S)}$ to about 1050 mAh/$g_{(S)}$, about 680 mAh/$g_{(S)}$ to about 1050 mAh/$g_{(S)}$, about 700 mAh/$g_{(S)}$ to about 1050mAh/$g_{(S)}$, about 720 mAh/$g_{(S)}$ to about 1050 mAh/$g_{(S)}$, about 740 mAh/$g_{(S)}$ to about 1050 mAh/$g_{(S)}$, about 760 mAh/$g_{(S)}$ to about 1050 mAh/$g_{(S)}$, about 780 mAh/$g_{(S)}$ to about 1050 mAh/$g_{(S)}$, about 800 mAh/$g_{(S)}$ to about 1050 mAh/$g_{(S)}$, about 820 mAh/$g_{(S)}$ to about 1050 mAh/$g_{(S)}$, about 840 mAh/$g_{(S)}$ to about 1050 mAh/$g_{(S)}$, about 860 mAh/$g_{(S)}$ to about 1050 mAh/$g_{(S)}$, about 880 mAh/$g_{(S)}$ to about 1050 mAh/$g_{(S)}$, about 900 mAh/$g_{(S)}$ to about 1050 mAh/$g_{(S)}$, about 950 mAh/$g_{(S)}$ to about 1050 mAh/$g_{(S)}$, or about 1000 mAh/$g_{(S)}$ to about 1050 mAh/$g_{(S)}$. In some embodiments, the specific capacity is limited to about 838 mAh/$g_{(S)}$.

In some embodiments, the 10 electron redox reaction between sulphur and/or its chemical species thereof is selected from:

$$S_{8(60\%)} \leftrightarrow S_8^{2-} \leftrightarrow S_6^{2-} \leftrightarrow S_4^{2-} \leftrightarrow S_3^{2-} \leftrightarrow S_2^{2-} \leftrightarrow S^{2-}_{(35\%)}$$

.

In some embodiments, when the battery is limited to a 10 electron redox reaction, the specific capacity is limited to about 650 mAh/$g_{(S)}$ to about 1,310 mAh/$g_{(S)}$. In other

embodiments, the specific capacity is limited to about 700 mAh/$g_{(S)}$ to about 1,310 mAh/$g_{(S)}$, about 720 mAh/$g_{(S)}$ to about 1,310 mAh/$g_{(S)}$, about 740 mAh/$g_{(S)}$ to about 1,310 mAh/$g_{(S)}$, about 760 mAh/$g_{(S)}$ to about 1,310 mAh/$g_{(S)}$, about 780 mAh/$g_{(S)}$ to about 1,310 mAh/$g_{(S)}$, about 800 mAh/$g_{(S)}$ to about 1,310 mAh/$g_{(S)}$, about 820 mAh/$g_{(S)}$ to about 1,310 mAh/$g_{(S)}$, about 840 mAh/$g_{(S)}$ to about 1,310 mAh/$g_{(S)}$, about 860 mAh/$g_{(S)}$ to about 1,310 mAh/$g_{(S)}$, about 700 mAh/$g_{(S)}$ to about 1,310 mAh/$g_{(S)}$, about 880 mAh/$g_{(S)}$ to about 1,310 mAh/$g_{(S)}$, about 900 mAh/$g_{(S)}$ to about 1,310 mAh/$g_{(S)}$, about 920 mAh/$g_{(S)}$ to about 1,310 mAh/$g_{(S)}$, about 940 mAh/$g_{(S)}$ to about 1,310 mAh/$g_{(S)}$, about 960 mAh/$g_{(S)}$ to about 1,310 mAh/$g_{(S)}$, about 980 mAh/$g_{(S)}$ to about 1,310 mAh/$g_{(S)}$, about 1000 mAh/$g_{(S)}$ to about 1,310 mAh/$g_{(S)}$, about 1020 mAh/$g_{(S)}$ to about 1,310 mAh/$g_{(S)}$, about 1040 mAh/$g_{(S)}$ to about 1,310 mAh/$g_{(S)}$, about 1060 mAh/$g_{(S)}$ to about 1,310 mAh/$g_{(S)}$, about 1080 mAh/$g_{(S)}$ to about 1,310 mAh/$g_{(S)}$, about 1100 mAh/$g_{(S)}$ to about 1,310 mAh/$g_{(S)}$, about 1150 mAh/$g_{(S)}$ to about 1,310 mAh/$g_{(S)}$, about 1200 mAh/$g_{(S)}$ to about 1,310 mAh/$g_{(S)}$, or about 1250 mAh/$g_{(S)}$ to about 1,310 mAh/$g_{(S)}$. In some embodiments, the specific capacity is limited to about 1,047 mAh/$g_{(S)}$.

In some embodiments, the 12 electron redox reaction between sulphur and/or its chemical species thereof is selected from:

$$S_8 \leftrightarrow S_8^{2-} \leftrightarrow S_6^{2-} \leftrightarrow S_4^{2-} \leftrightarrow S_3^{2-} \leftrightarrow S_2^{2-} \leftrightarrow S^{2-}{}_{(50\%)}$$

.

The reaction from $S_8 \leftrightarrow S_2^{2-}$ provides 8 electrons while $S_2^{2-} \leftrightarrow S^{2-}{}_{(50\%)}$ provides another 4 electrons.

In some embodiments, when the battery is limited to a 12 electron redox reaction, the specific capacity is limited to about 940 mAh/$g_{(S)}$ to about 1570 mAh/$g_{(S)}$. In other embodiments, the specific capacity is limited to about 960 mAh/$g_{(S)}$ to about 1570 mAh/$g_{(S)}$, about 980 mAh/$g_{(S)}$ to about 1570 mAh/$g_{(S)}$, about 1000 mAh/$g_{(S)}$ to about 1570 mAh/$g_{(S)}$, about 1020 mAh/$g_{(S)}$ to about 1570 mAh/$g_{(S)}$, about 1040 mAh/$g_{(S)}$ to about 1570 mAh/$g_{(S)}$, about 1060 mAh/$g_{(S)}$ to about 1570 mAh/$g_{(S)}$, about 1080 mAh/$g_{(S)}$ to about 1570 mAh/$g_{(S)}$, about 1100 mAh/$g_{(S)}$ to about 1570 mAh/$g_{(S)}$, about 1120 mAh/$g_{(S)}$ to about 1570 mAh/$g_{(S)}$, about 1140 mAh/$g_{(S)}$ to about 1570 mAh/$g_{(S)}$, about 1160 mAh/$g_{(S)}$ to about 1570 mAh/$g_{(S)}$, about 1180 mAh/$g_{(S)}$ to about 1570 mAh/$g_{(S)}$, about 1200 mAh/$g_{(S)}$ to about 1570 mAh/$g_{(S)}$, about 1220 mAh/$g_{(S)}$ to about

1570 mAh/$g_{(S)}$, about 1240 mAh/$g_{(S)}$ to about 1570 mAh/$g_{(S)}$, about 1260 mAh/$g_{(S)}$ to about 1570 mAh/$g_{(S)}$, about 1280 mAh/$g_{(S)}$ to about 1570 mAh/$g_{(S)}$, about 1300 mAh/$g_{(S)}$ to about 1570 mAh/$g_{(S)}$, about 1320 mAh/$g_{(S)}$ to about 1570 mAh/$g_{(S)}$, about 1340 mAh/$g_{(S)}$ to about 1570 mAh/$g_{(S)}$, about 1360 mAh/$g_{(S)}$ to about 1570 mAh/$g_{(S)}$, about 1380 mAh/$g_{(S)}$ to about 1570 mAh/$g_{(S)}$, about 1400 mAh/$g_{(S)}$ to about 1570 mAh/$g_{(S)}$, about 1440 mAh/$g_{(S)}$ to about 1570 mAh/$g_{(S)}$, about 1480 mAh/$g_{(S)}$ to about 1570 mAh/$g_{(S)}$, or about 1520 mAh/$g_{(S)}$ to about 1570 mAh/$g_{(S)}$. In some embodiments, the specific capacity is limited to about 1,256 mAh/$g_{(S)}$.

The method also limits a charge and/or discharge voltage of the battery based on a rate of change of voltage relative to an electric parameter of the battery. It was found that the rate of change can represent an onset and/or end of redox reactions between sulphur and/or its chemical species thereof. In particular, when the rate of change varies between positive and negative values, it signifies a transition between redox reactions.

In some embodiments, the limit of the charge and/or discharge voltage of the battery is adjustable in a stepwise manner based on the type of redox reactions between sulphur and/or its chemical species thereof.

In some embodiments, the limit of the charge and/or discharge specific capacity of the battery is adjustable in real time during operation of the battery.

In some embodiments, the voltage is limited based on a rate of change of charge relative to voltage. In some embodiments, the rate of change of charge relative to voltage is a first order derivative of a current-voltage function.

In some embodiments, the voltage is limited based on a negative peak in a first order derivative of a current-voltage function. In some embodiments, the current-voltage function is obtained from a cyclic voltammetry measurement.

In some embodiments, the rate of change of charge relative to voltage is a second order derivative of a capacity-voltage function.

In some embodiments, the voltage is limited based on an intersect of extrapolated tangents at a deflection point or inflection point of a capacity-voltage function. In some

embodiments, the voltage is limited based on a negative peak in a second order derivative of a capacity-voltage function. In some embodiments, the capacity-voltage function is obtained from a galvanic charge (GChg) plot.

The lower voltage limit may be the discharge cut-off voltage. This value may be obtained or calculated following the method as described herein.

In some embodiments, when the battery is limited to a 6 electron redox reaction, the charge voltage is limited to about 2.3 V to about 2.5 V. In some embodiments, when the battery is limited to a 6 electron redox reaction, the charge voltage is limited to about 2.33 V or about 2.42 V.

In some embodiments, when the battery is limited to a 8 electron redox reaction, the charge voltage is limited to about 2.3 V to about 2.4 V. In some embodiments, when the battery is limited to a 8 electron redox reaction, the charge voltage is limited to about 2.33 V or about 2.37 V.

In some embodiments, when the battery is limited to a 10 electron redox reaction, the charge voltage is limited to about 2.3 V to about 2.4 V. In some embodiments, when the battery is limited to a 10 electron redox reaction, the charge voltage is limited to about 2.37 V.

In some embodiments, the battery has a charge capacity limit of about 1,047 mAh/$g_{(S)}$ and a charge voltage limit of 2.4 V. In other embodiments, the battery has a charge capacity limit of about 1,047 mAh/$g_{(S)}$, a charge voltage limit of about 2.4 V and a discharge voltage limit of about 1.8 V.

In some embodiments, the battery has a charge capacity limit of about 838 mAh/$g_{(S)}$ and a charge voltage limit of about 2.3 V to about 2.4 V. In other embodiments, the battery has a charge capacity limit of about 838 mAh/$g_{(S)}$, a charge voltage limit of about 2.3 V to about 2.4 V and a discharge voltage limit of 1.8 V. In other embodiments, the battery has a charge capacity limit of about 838 mAh/$g_{(S)}$, a charge voltage limit of about 2.3 V to about 2.4 V and a discharge capacity limit of about 838 mAh/$g_{(S)}$.

In some embodiments, the battery has a charge capacity limit of about 628 mAh/$g_{(S)}$ and a charge voltage limit of about 2.3 V to about 2.5 V. In other embodiments, the battery has a charge capacity limit of about 628 mAh/$g_{(S)}$, a charge voltage limit of about 2.3 V to about 2.5 V, and a discharge voltage limit of 1.8 V. In other embodiments, the battery has a charge capacity limit of about 628 mAh/$g_{(S)}$, a charge voltage limit of about 2.3 V to about 2.5 V, and a discharge capacity limit of 628 mAh/$g_{(S)}$.

In some embodiments, the sulphur based battery is an alkali metal-sulfur battery, alkaline-earth metal-sulfur battery, alloy-sulfur battery, or a metal-sulfur battery wherein the metal is selected from aluminium, vanadium, titanium, molybdenum, iron, niobium, or tungsten.

In some embodiments, the alkali metal is selected from Li, Na, K, or a combination thereof. In some embodiments, the battery is a Li-S battery.

In some embodiments, the alkaline-earth metal is selected from Mg, Ca, Sr, Ba, or a combination thereof.

In some embodiments, the alloy is selected from Li-Sn, Li-Mg, Li-B, Fe-Co, Li-Si, Li-Hg, Li-Al, sodium alloy, aluminium alloy, potassium alloy and magnesium alloy.

The energy density (Wh/L) refers to the nominal battery energy per unit volume, sometimes referred to as the volumetric energy density. Specific energy is a characteristic of the battery chemistry and packaging. Along with the energy consumption of the vehicle, it determines the battery size required to achieve a given electric range.

A depth of discharge (DOD) (%) is the percentage of battery capacity that can be discharged expressed as a percentage of maximum capacity. In some embodiments, the battery is characterised by a DOD of at least about 95%. In other embodiments, the DOD is at least about 90%, about 85%, about 80%, about 75%, about 70%, about 65%, about 60%, about 55%, about 50%, about 40%, about 30%, or about 20%.

In some embodiments, when the battery is limited to a 6 electron redox reaction, the battery is characterised by a DOD of about 35% to about 40%. In other embodiments, the battery is characterised by a DOD of about 37.5%.

In some embodiments, when the battery is limited to a 8 electron redox reaction, the battery is characterised by a DOD of about 45% to about 55%. In other embodiments, the battery is characterised by a DOD of about 50%.

In some embodiments, when the battery is limited to a 10 electron redox reaction, the battery is characterised by a DOD of about 60% to about 70%. In other embodiments, the battery is characterised by a DOD of about 62.5%.

In some embodiments, when the battery is limited to a 12 electron redox reaction, the battery is characterised by a DOD of about 70% to about 80%. In other embodiments, the battery is characterised by a DOD of about 75%.

Cycle life refers to the number of discharge-charge cycles the battery can experience before it fails to meet specific performance criteria. Cycle life is estimated for specific charge and discharge conditions. The actual operating life of the battery is affected by the rate and depth of cycles and by other conditions such as temperature and humidity. In general, the higher the DOD, the lower the cycle life.

In some embodiments, the battery is characterised by a cycle life of at least about 20 cycles. In other embodiments, the cycle life is at least about 30 cycles, about 40 cycles, about 50 cycles, or about 60 cycles.

The present invention also provides a battery management system, comprising:

a) limiting a charge and/or discharge specific capacity of the battery based on

$$specific\ capacity\ (limit) = total\ specific\ capacity \times \frac{n}{16}$$

wherein the total specific capacity is the specific capacity of the battery derived from complete charging and/or discharging; and

n is a number of electrons transferred in redox reactions between sulphur and/or its chemical species thereof; and

b) limiting a charge and/or discharge voltage of the battery based on a rate of change of voltage relative to an electric parameter of the battery, in which the

rate of change represents a transition between redox reactions of sulphur and/or its chemical species thereof.

In some embodiments, the battery management system is configured to:

a) limit a charge and/or discharge specific capacity of the battery based on

$$specific\ capacity\ (limit) = total\ specific\ capacity \times \frac{n}{16}$$

wherein the total specific capacity is the specific capacity of the battery derived from complete charging and/or discharging; and

n is a number of electrons transferred in redox reactions between sulphur and/or its chemical species thereof; and

b) limit a charge and/or discharge voltage of the battery based on a rate of change of voltage relative to an electric parameter of the battery, in which the rate of change represents a transition between redox reactions of sulphur and/or its chemical species thereof.

In some embodiments, the limit of the charge and/or discharge specific capacity of the battery is adjustable in a stepwise manner based on the number of electrons transferred in redox reactions between sulphur and/or its chemical species thereof.

In some embodiments, the limit of the charge and/or discharge specific capacity of the battery is adjustable in real time during operation of the battery.

In some embodiments, the limit of the charge and/or discharge voltage of the battery is adjustable in a stepwise manner based on the type of redox reactions between sulphur and/or its chemical species thereof.

In some embodiments, the limit of the charge and/or discharge voltage of the battery is adjustable in real time during operation of the battery.

In some embodiments, the limit to the specific capacity and/or voltage is adjustable by a control means. The control means can be an electric control means. The control means can be adjust the limits automatically depending on the charge state of the battery.

In some embodiments, the limit to the specific capacity and/or voltage is adjustable by a user.

Operation of a battery based on the number of electron given/released by the electrochemical reactions prevents overcharging by preventing polysulfide shuttling and reduces capacity degradation in sulphur based battery. Further, controlled formation of the intermediary electrochemical species by limiting the capacities and/or voltages during battery' charge and discharge improves cycle life, capacity retention, and Coulombic efficiency during cycling of alkali and alkaline-earth metals/alloys-sulfur batteries.

The method for controlling the formation of the intermediary electrochemical species by the first order derivative (1^{st} DCV) of the current as a function of voltage (obtained from the cyclic voltammetry tests), or from the second order derivative (2^{nd} DCV) of the capacity as a function of voltage (obtained from the galvanic charge tests), allows the programming of battery management systems to operate battery packs made-up of alkali and alkaline-earth metals/alloys-sulfur batteries. Methods for controlling the formation of the intermediary electrochemical species by extrapolated tangents allows the quick adjust of battery tests on alkali and alkaline-earth metals/alloys-sulfur batteries.

The disclosed method can be used in battery management systems (BMS) to operate battery packs made-up of alkali and alkaline-earth metals/alloys-sulfur batteries. The disclosed method can also be used for developing test-kits/equipment/standards/procedures to test the life of alkali and alkaline-earth metals/alloys-sulfur batteries.

The BMS can record the data (such as voltage, current, time, capacity) for the plots, which can then be plotted for finding the tangent in real time or direct data analysis using data analytic tools can be done to obtain the values of the onset and endset values of inflection on the galvanic charge data. Data analysis tools can be incorporated within the BMS for various real-time analytics. Further, machine learning or AI based approaches can also be used to predict these values for forthcoming cycles which could be used to predict a lot of performance parameters like cycle life, rate capability, and cell failures. These intelligent systems can be used in EV or battery pack chargers, which could be used to diagnose, record and predict the state of health of the batteries every time the batteries are being charged.

As examples, the performance of Li-S cells fabricated using Li metal as the counter and the reference electrode and using prevailing ether based electrolytes under different operation methods was demonstrated. The configuration of the cells was kept as standard as possible in relation to the composition of the cathode, the active material mass loading, the composition of the electrolyte (no-additives were used), the electrolyte/sulphur ratio, etc., to evaluate essentially the differences obtained by changing the operation methods and not specifics to the cell configurations.

As an example of typical Li-S cell, a cell was discharged until 1.0 V at 0.05 current-rate to evaluate the complete discharge pattern. The cell provided an initial specific capacity of ~1,675 mAh/$g_{(S)}$ (Figure 1), what correspond to ~100% sulfur utilization. The Li-S cell delivered a discharge capacity correspondent to a 16 electron redox reaction, with 8 electrons coming from the first two phase reactions (solid-liquid and liquid–solid) and the remaining 8 electrons from the last phase reaction (solid-solid).

Method for controlling the formation of intermediary polysulfide species

A method to control the formation of polysulfide species during cell charging uses capacity and/or voltage as the limiting factors. The specific capacity limit is calculated based on the number of electrons to form specific polysulfide species. Considering the complete electrochemical charge/discharge reactions as a 16 electron reactions that deliver ~1,675 mAh/$g_{(S)}$ (Figure 1), each electron will deliver ~104.6875 mAh/$g_{(S)}$. Consequently, as examples, a 12-, 10-, 8-, and 6-electron operations would result in specific charge capacities of ~1,256.3 mAh/$g_{(S)}$, ~1,046.9 mAh/$g_{(S)}$, ~837.5 mAh/$g_{(S)}$, and ~628.1 mAh/$g_{(S)}$, respectively. The setting of a capacity limit for charging helps prevent cell overcharging caused by a variety of reasons.

The voltage limit is calculated based on the first order derivative of current as a function of voltage obtained from the cyclic voltammetry tests, or from the second order derivative of capacity as a function of voltage obtained from the galvanic charge (GChg) tests (example at Figure 2), or by extrapolating the tangents on the inflection to find the onset and endset on the galvanic charge curve (similar to the procedure commonly used for evaluate data from thermos-analysis, e.g. ASTM E2550−17), example at Figure 3.

The voltage can be affected by the current rate and cell impedance. Therefore, the voltage limits should be determined for the same current rates in which the cell will operate (example at Figure 3). In cases where the voltage limits are determined only for lower rates, a factor related to the difference between the over potentials should be added.

For example, considering the GChg at 0.2 current rate obtained for a specific Li-S cell (presented in the Figure 2), to mainly form Li_2S_2, Li_2S_4, Li_2S_6, Li_2S_8, and S_8 the charging voltage limit should be ~2.240 V, ~2.290 V, ~2.335 V, ~2.370 V, and ~2.420 V respectively.

The charging will finish once the capacity or voltage limit is reached.

Typically, the cells undergo a formation process before cycling, which can include or not the method disclosed here for charging. The formation process is a process carried out a very low rate of 0.05C or 0.01C where the cell is discharged and charged between a pre-set voltage limits which can follow the voltage limits as mentioned in this work.

Voltage limit obtained by derivative methods

The voltage limit can be determined based on the first order derivative of current as a function of voltage obtained from the cyclic voltammetry tests, or from the second order derivative of capacity as a function of voltage obtained from the galvanic charge (GChg) tests.

The voltage limit can be determined on the derivative curve by the negative peaks (trough), which represent the endset of a specific electrochemical event or the endset of a maximum electrochemical transformation event (Figure 2).

Voltage limit obtained by extrapolated tangents method

The onset voltage limits are determined by selecting a point on the capacity as a function of voltage curve from GChg tests where a deflection is first observed from the established baseline prior to the change on the curve inflection and extrapolating a tangent line from this selected point and another from the baseline, the point where the tangents cross determine the onset (example at Figure 3).

The endset voltage limits are determined by selecting a point on the capacity as a function of voltage curve from GChg tests where a deflection is first observed from the established baseline subsequent to the change on the curve inflection and extrapolating a tangent line from this point and another from the baseline, the point where the tangents cross determine the endset.

Another way for selecting the points from where the tangents will origin is using the positive and negative peaks from the first order derivative of the capacity as a function of voltage curve obtained from the GChg tests.

Preferably, the galvanic charge curve can be zoomed to a scale that allows the clear identification of the change on the curve inflection for the onset or endset voltages determination.

Examples of the disclosed method for controlling the formation of intermediary polysulfide species

A method comprised of constant-current and constant-voltage (CCCV) charging protocol with capacity and voltage as the limiting factors was used to ensure the completion of the redox reactions even at high rates.

10-electron operations with charge capacity limit of 1,046.9 mAh/$g_{(S)}$, charge voltage limit of 2.37 V, and discharge voltage limit of 1.8 V is shown in Figure 4.

$$S_{8(60\%)} \leftrightarrow Li_2S_8 \leftrightarrow Li_2S_6 \leftrightarrow Li_2S_4 \leftrightarrow Li_2S_3 \leftrightarrow Li_2S_2 \leftrightarrow Li_2S_{(\sim 35\%)}$$

8-electron operations with charge capacity limit of 837.5 mAh/$g_{(S)}$, charge voltage limit of 2.335 V, and discharge voltage limit of 1.8 V is shown in Figure 4.

$$Li_2S_6 \leftrightarrow Li_2S_4 \leftrightarrow Li_2S_3 \leftrightarrow Li_2S_2 \leftrightarrow Li_2S_{(\sim 35\%)}$$

8-electron operations with charge capacity limit of 837.5 mAh/$g_{(S)}$, charge voltage limit of 2.38 V, and discharge capacity limit of 837.5 mAh/$g_{(S)}$.

$$S_8 \leftrightarrow Li_2S_8 \leftrightarrow Li_2S_6 \leftrightarrow Li_2S_4 \leftrightarrow Li_2S_{2\text{-}3}$$

6-electron operations with charge capacity limit of 628.1 mAh/$g_{(S)}$, charge voltage limit of 2.325 V, and discharge voltage limit of 1.8 V is shown in Figure 4.

$$Li_2S_{6(\sim 75\%)} \leftrightarrow Li_2S_4 \leftrightarrow Li_2S_3 \leftrightarrow Li_2S_2 \leftrightarrow Li_2S_{(\sim 35\%)}$$

6-electron operations with charge capacity limit of 628.1 mAh/$g_{(S)}$, charge voltage limit of 2.425 V, and discharge capacity limit of 628.1 mAh/$g_{(S)}$.

$$S_8 \leftrightarrow Li_2S_8 \leftrightarrow Li_2S_6 \leftrightarrow Li_2S_4$$

The percentages indicated for the polysulfides are related to their electron contribution, which is the transformation of a species undergoing redox conversion thereby producing the said number of electrons. The remaining amount stay as un-reactive species.

Each step of CCCV charging finish once the capacity limit is reached. If the cell does not reach the capacity limit until the set upper voltage limit, then a constant-voltage charging continues till the current is reduced, until, for example, 1 A/$g_{(S)}$, or the capacity limit is reached.

As examples of application of the method for controlling the formation of intermediary polysulfide species, the different protocols for 10-, 8-, and 6-electron reaction (described in details above) were evaluated and compared to a standard protocol (~12-electrons) that uses constant-current (CC) with cut-off charge voltage of 2.8 V and no charge capacity limit. The discharge of all the Li-S cells were carried out under a constant-current (CC) until the cut-off voltage of 1.4 V at 0.2 current rate. All the cells undergo a formation cycle before cycling evaluation. The formation cycle starts with a CC discharge till cut-off voltage at 0.05 current rate followed by a CC or CCCV protocol charge.

The capacity degradation plot (Figure 4) of Li-S cells shows the better capacity retention of the cells operated with the method disclosed in comparison with the standard-protocol.

In Figure 4, the discharge of the Li-S cell was carried out under a constant-current (CC) protocol with discharge voltage limit of 1.8 V was set to prevent electrolyte degradation. With the use of electrolytes stable at voltage potentials below 1.8 V, this limit can be lowered up to 1.0 V.

During a redox reaction, by limiting the operation (charge-discharge) of the cell to the number of electrons transferred per S_8 molecule present in the cathode, can be

controlled. This strategy improves the cycle life of the battery at the cost of energy density. Such an approach can help design and build battery pack modules with Li-S cells along with a battery management system where the life of a battery can be improved following the methods as disclosed in this invention.

It will be appreciated that many further modifications and permutations of various aspects of the described embodiments are possible. Accordingly, the described aspects are intended to embrace all such alterations, modifications, and variations that fall within the spirit and scope of the appended claims.

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

Throughout this specification and the claims which follow, unless the context requires otherwise, the phrase "consisting essentially of", and variations such as "consists essentially of" will be understood to indicate that the recited element(s) is/are essential i.e. necessary elements of the invention. The phrase allows for the presence of other non-recited elements which do not materially affect the characteristics of the invention but excludes additional unspecified elements which would affect the basic and novel characteristics of the method defined.

The reference in this specification to any prior publication (or information derived from it), or to any matter which is known, is not, and should not be taken as an acknowledgment or admission or any form of suggestion that that prior publication (or information derived from it) or known matter forms part of the common general knowledge in the field of endeavour to which this specification relates.

Claims

1. A method of charging and/or discharging a sulphur-based battery, comprising:

a) limiting a charge and/or discharge specific capacity of the battery based on

$$specific\ capacity\ (limit) = practical\ specific\ capacity \times \frac{n}{16}$$

wherein the practical specific capacity is the specific capacity of the battery derived from complete charging and/or discharging; and

n is a number of electrons transferred in redox reactions between sulphur and/or its chemical species thereof; and

b) limiting a charge and/or discharge voltage of the battery based on a rate of change of voltage relative to an electric parameter of the battery, in which the rate of change represents a transition between redox reactions of sulphur and/or its chemical species thereof;

wherein the limit of the charge and/or discharge specific capacity of the battery is adjustable in a stepwise manner based on the number of electrons transferred in redox reactions between sulphur and/or its chemical species thereof; and

wherein the limit of the charge and/or discharge voltage of the battery is adjustable in a stepwise manner based on the type of redox reactions between sulphur and/or its chemical species thereof.

2. The method according to claim 1, wherein the limit of the charge and/or discharge specific capacity of the battery is adjustable in real time during operation of the battery.

3. The method according to claim 1 or 2, wherein n is an even number.

4. The method according to any one of claims 1 to 3, wherein when the practical specific capacity is 1,675 mAh/g$_{(S)}$, each electron transfer is characterised by a specific capacity of 104.69 mAh/g$_{(S)}$.

5. The method according to any one of claims 1 to 4, wherein the redox reactions are selected from one of the following:

when n is 6, the 6 electron redox reaction between sulphur and/or its chemical species thereof is selected from:

$$S_6^{2-}{}_{(\sim 75\%)} \leftrightarrow S_4^{2-} \leftrightarrow S_3^{2-} \leftrightarrow S_2^{2-} \leftrightarrow S^{2-}{}_{(\sim 35\%)}$$

$$S_8 \leftrightarrow S_8^{2-} \leftrightarrow S_6^{2-} \leftrightarrow S_4^{2-}$$

wherein when the battery is limited to a 6 electron redox reaction, the specific capacity is limited to 35% to 40% of the practical specific capacity;

when n is 8, the 8 electron redox reaction between sulphur and/or its chemical species thereof is selected from:

$$S_6^{2-} \leftrightarrow S_4^{2-} \leftrightarrow S_3^{2-} \leftrightarrow S_2^{2-} \leftrightarrow S^{2-}_{(\sim 35\%)}$$

$$S_8 \leftrightarrow S_8^{2-} \leftrightarrow S_6^{2-} \leftrightarrow S_4^{2-} \leftrightarrow S_{2\text{-}3}^{2-}$$

wherein the specific capacity is limited to 45% to 55% of the practical specific capacity;

when n is 10, the 10 electron redox reaction between sulphur and/or its chemical species thereof is selected from:

$$S_{8(60\%)} \leftrightarrow S_8^{2-} \leftrightarrow S_6^{2-} \leftrightarrow S_4^{2-} \leftrightarrow S_3^{2-} \leftrightarrow S_2^{2-} \leftrightarrow S^{2-}_{(35\%)}$$

wherein the specific capacity is limited to 60% to 70% of the practical specific capacity;

when n is 12, the 12 electron redox reaction between sulphur and/or its chemical species thereof is selected from:

$$S_8 \leftrightarrow S_8^{2-} \leftrightarrow S_6^{2-} \leftrightarrow S_4^{2-} \leftrightarrow S_3^{2-} \leftrightarrow S_2^{2-} \leftrightarrow S^{2-}_{(50\%)}$$

wherein the specific capacity is limited to 70% to 80% of the practical specific capacity.

6. The method according to any one of claims 1 to 5, wherein the limit of the charge and/or discharge voltage of the battery is adjustable in real time during operation of the battery.

7. The method according to any one of claims 1 to 6, wherein the voltage is limited based on a rate of change of charge relative to voltage;

wherein the rate of change of charge relative to voltage is a first order derivative of a current-voltage function, wherein the voltage is limited based on a negative peak in a first order derivative of a current-voltage function.

8. The method according to claim 7, wherein the current-voltage function is obtained from a cyclic voltammetry measurement.

9. The method according to any one of claims 1 to 6 , wherein the voltage is limited based on a rate of change of charge relative to voltage;

wherein the rate of change of charge relative to voltage is a second order derivative of a capacity-voltage function, wherein the voltage is limited based on a negative peak in a second order derivative of a capacity-voltage function.

10. The method according to claim 9, wherein the voltage is limited based on an intersect of extrapolated tangents at a deflection point or inflection point of a capacity-voltage function;
wherein the capacity-voltage function is obtained from a galvanic charge (GChg) plot.

11. The method according to any one of claims 1 to 10, wherein when the battery is limited to a 6 electron redox reaction, the charge voltage is limited to 2.3 V to 2.5 V or preferably 2.33 V or 2.42 V;
wherein when the battery is limited to an 8 electron redox reaction, the charge voltage is limited to 2.3 V to 2.4 V or preferably 2.33 V or 2.37 V; and
wherein when the battery is limited to a 10 electron redox reaction, the charge voltage is limited to 2.3 V to 2.4 V or preferably 2.37 V.

12. The method according to any one of claims 1 to 11, wherein the sulphur-based battery is an alkali metal-sulfur battery, alkaline-earth metal-sulfur battery, alloy-sulfur battery, or a metal-sulfur battery wherein the metal is selected from aluminium, vanadium, titanium, molybdenum, iron, niobium, or tungsten.

13. The method according to claim 12, wherein the alkali metal is selected from Li, Na, K, or a combination thereof.

14. The method according to claim 12, wherein the alkaline-earth metal is selected from Mg, Ca, Sr, Ba, or a combination thereof.

15. The method according to claim 12, wherein the alloy is selected from Li-Sn, Li-Mg, Li-B, Fe-Co, Li-Si, Li-Hg, Li-Al, sodium alloy, aluminium alloy, potassium alloy and magnesium alloy.

16. A battery management system, wherein the battery management system is configured to:

a) limit a charge and/or discharge specific capacity of the battery based on

$$specific\ capacity\ (limit) = practical\ specific\ capacity \times \frac{n}{16}$$

wherein the practical specific capacity is the specific capacity of the battery derived from complete charging and/or discharging; and

n is a number of electrons transferred in redox reactions between sulphur and/or its chemical species thereof; and

b) limit a charge and/or discharge voltage of the battery based on a rate of change of voltage relative to an electric parameter of the battery, in which the rate of change represents a transition between redox reactions of sulphur and/or its chemical species thereof;

wherein the limit of the charge and/or discharge specific capacity of the battery is adjustable in a stepwise manner based on the number of electrons transferred in redox reactions between sulphur and/or its chemical species thereof; and

wherein the limit of the charge and/or discharge voltage of the battery is adjustable in a stepwise manner based on the type of redox reactions between sulphur and/or its chemical species thereof.

17. The battery management system according to claim 16, wherein the limit of the charge and/or discharge specific capacity of the battery is adjustable in a stepwise manner based on the number of electrons transferred in redox reactions between sulphur and/or its chemical species thereof.

18. The battery management system according to claim 16 or 17, wherein the limit of the charge and/or discharge voltage of the battery is adjustable in a stepwise manner based on the type of redox reactions between sulphur and/or its chemical species thereof.

19. The battery management system according to any one of claims 16 to 18, wherein the limit to the specific capacity and/or voltage is adjustable by a control means.

20. The battery management system according to any one of claims 16 to 19, wherein the limit to the specific capacity and/or voltage is adjustable by a user.