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(54) Title: MULTIFUNCTIONAL CATHODE ADDITIVES FOR BATTERY TECHNOLOGIES

(57) Abstract: A post-activation anode and a cathode containing a cathode additive that forms a conducting metal sulfide following activation of the cell of a battery cell system. The cathode additive may provide excess lithium to the anode and may compensate for lithium loss during the formation of a solid electrolyte interface upon contact between the deposited lithium and the electrolyte at the anode.

TITLE:

MULTI FUNCTIONAL CATHODE ADDITIVES FOR BATTERY TECHNOLOGIES

Cross Reference to Related Application

[0001] This application claims priority to provisional application number 61/940,976, filed February 18, 2014, entitled "Dual Function Cathode Additives for Battery Technologies", the entirety of which is hereby incorporated by reference in their entirety.

STATEMENT OF GOVERNMENT RIGHTS

[0002] This invention was made with Government support under contract numbers DE-AC02-98CH10886 and DE-SC0012704 awarded by the U.S. Department of Energy. The Government has certain rights in the invention.

I. FIELD OF THE INVENTION

[0003] This disclosure relates generally to additive compounds for use in lithium-sulfur or lithium-ion batteries. In particular, it relates to cathode additive compounds which may be used to form an anode *in situ*, supply extra lithium for the anode or improve cathode electronic conductivity in high density batteries or rechargeable batteries.

II. BACKGROUND

[0004] Lithium ion batteries are used as power sources for consumer electronics, including laptops, tablets, and smart phones. The amount of energy stored by weight and/or volume is one way to measure performance in these applications. For larger applications, such as for example electric vehicles, power density may be measured. The batteries should be able to charge and discharge quickly as they react to sudden changes in load during actual driving conditions.

[0005] In the case of a traditional lithium ion battery, the lithium salt may be one that is capable of dissociating lithium ions and anions. During the discharging process the lithium ions from the anode pass through the electrolyte to the electrochemically-active material of the cathode where the ions are taken up or absorbed with simultaneous release of electrical energy. During the charging process the lithium ion flow is reversed so that lithium ions pass from the electrochemically-active cathode material through the electrolyte and are returned to the anode.

[0006] The high cost of lithium or Li-ion battery technologies is slowing their adoption. Research efforts to lower their cost have been in two major areas, namely reducing the material cost and lowering the manufacturing cost. Material cost may be controlled by the choice of electrochemical system, while manufacturing cost is dependent on the processes used to prepare the battery components and for the cell assembly. A lithium-sulfur electrochemical couple system has the potential to lower the material cost due to the abundance of sulfur in nature and at the same time boost the energy density of the cell system due to the use of lithium metal to replace graphite in current benchmark Li-ion batteries.

[0007] Lithium-sulfur (Li-S) batteries use a sulfur-based compound having a sulfur-sulfur bond (often referred to as an “active sulfur”) as a positive active material, and a lithium metal or a carbon-based compound as a negative active material. Upon discharge (electrochemical reduction), a sulfur-sulfur bond is broken, and results in a decrease in the oxidation number of sulfur (S). When recharging (electrochemical oxidation), a sulfur-sulfur bond is formed, and this leads to an increase in the oxidation number of S. As a result, electrochemical energy can be stored and generated using the cycling reduction-oxidation reactions.

[0008] Additional lithium is required for a Li-S battery (and Li-ion battery) because of the inefficiencies in lithium cycling, including the anode SEI (solid electrolyte interface) formation. Introducing extra lithium into the cell system without using lithium metal and maintaining high cathode energy utilization continues to be a challenge for the development of Li-ion batteries. One current approach for Li-ion battery is to use extra cathode material as the source of additional lithium. However, this may cause the utilization of the cathode to be lower. Further, a significant amount of the electrochemically inactive carbon black (up to 15+%) is used as a cathode conductive additive, which reduces the cathode volumetric energy density due to its low density. Since lithium metal is a reactive material towards humidity and air, special environmental control, such as a dry room or glove box, is used for material processing which can increase the cost associated with the lithium metal anode battery manufacturing.

[0009] One challenge to an anodeless lithium battery design concept is that the activated cell is anode limited. No extra lithium exists in the anode. In a typical battery the anode is one of the two electrodes that supplies electrons by virtue of an oxidation process occurring at that one of the two electrodes (“anodic process”). In contrast, the other of the two electrodes is a cathode and this other electrode consumes electrons by virtue of a reduction process occurring that other of the two electrodes (“cathodic process”).

[0010] Due to the formation of the SEI layer on the lithium metal (or lithium intercalated graphite, or lithium-silicon alloy) surface during the activation, part of the lithium from the cathode may be consumed (irreversible capacity) and converted into the insoluble lithium salt as part of the SEI layer. Therefore, the cathode utilization may be lower (<100%) in the subsequent cell cycling. Thus, the conventional lithium rechargeable cell design is not typically anodeless and extra lithium is used to compensate the inefficiency of the lithium cycling. As it is undesirable to handle and manufacture a lithium metal anode due to its high reactivity, for an anodeless cell design, it is desirable to be able to supply extra lithium into the cell system to compensate for the low cycling coulombic efficiency of lithium anode without using lithium metal while still maintaining high utilization of cathode in the subsequent cell cycling.

[0011] The concept of anodeless rechargeable lithium cell designs have other technical challenges such as for example, anode limiting cell balance, introducing extra lithium into the anodeless cell design and maintaining high cathode utilization in subsequent cycles without the use of lithium metal while maintaining power capability and costs of production.

[0012] Therefore, there is a need for a low cost Li metal anode/cell manufacturing process, its use with the anodeless concept, and the use of multi functional cathode additive compounds for lithium or lithium-ion batteries with improved capabilities.

[0013] There is the possibility that an anodeless cell design could eliminate the use of lithium metal in the cell manufacturing process steps which may help to maintain a lower manufacturing cost. Therefore, there is a need to introduce excess lithium into an anodeless cell system to compensate for low cycling coulumbic efficiency of lithium anode without using lithium metal due to its high reactivity and maintain high utilization of cathode in the subsequent cell cycling.

SUMMARY

[0014] This disclosure provides embodiments of a cathode additive in an anodeless or anode containing battery cell system and design that can be used in high energy density batteries or rechargeable batteries such as for example, Li batteries such as lithium-sulfur (Li-S) or lithium-ion batteries, or sodium-sulfur (Na-S) batteries. In the present battery cell system, extra lithium may be for example formed *in situ* into a rechargeable Li-S battery for an enhanced cycle life to compensate for the lithium lost due to low cycling coulombic efficiency.

[0015] The battery cell design has a cathode that may supply lithium in the cell system during cell activation. An example can be shown with a Li-S cell, in equation 1.

$$Li_2S \text{ (Cathode) } \text{---}\!\!\rightarrow \text{ Li (anode) + S (Cathode)} \qquad (1)$$

[0016] In equation 1, Li_2S is the cathode precursor material or cathode additive prior to cell activation, and during activation electrons may flow from the cathode to the anode through an external circuit. The cathode additive, Li_2S may be oxidized to form S on the cathode and the lithium ion may migrate from the cathode through the electrolyte to the anode current collector before an anode is present, or to the lithium metal or coated graphite, silicon composite or other anode materials when there is an anode present. When the lithium ion migrates it may be reduced and result in a lithium metal deposition on the anode current collector. When the cell is discharged the reverse reaction of equation 1 may deliver the cell energy to the targeted working loads such as an electric vehicle, or other electronic device.

[0017] The present cathode additive may be an initial metal sulfide compound that contains for example Li and may be used with a sulfur cathode. In one embodiment, the cathode additive may form excess Li. Upon cell activation, the first time the lithium battery is charged, the sulfur cathode may undergo an irreversible reaction to form a Li metal deposited at the anode. Secondary batteries undergo an irreversible reaction when they are first charged, or activated. In the case of the Li-S battery technology, the cathode additive containing lithium may be formed into a Li_2S cathode when the battery is assembled. During the first charging cycle, the cathode undergoes oxidation, and may liberate Li ions that form a post-activation anode while the conducting metal sulfide is left at the cathode. Therefore, before activation the lithium battery may be anodeless.

[0018] The anode may be formed after the cell is activated (i.e., post-activation). After activation by the first charging cycle, the cell works like any other Li or Li-ion battery and undergoes no further irreversible reactions. The excess Li may be able to compensate for Li loss during the formation of a solid electrolyte interface (SEI) upon contact between the deposited Li and the electrolyte at the anode. Further, the cathode additive when it is delithiated may act as a conductive additive to the cathode. Further still, the cathode additive may contribute to the reduction of polysulfide dissolution in the electrolyte.

[0019] The present battery cell system may comprise a cathode, an anode or an anode formed *in situ*, a separator between the cathode and the anode or the anode current collector before the anode is formed *in situ*, and an electrolyte. The cathode comprises a cathode additive or a conductive additive. The cathode additive may be a lithium containing compound that may be delithiated to supply lithium to form an anode *in situ*. In addition, the cathode additive may be delithiated to form the conductive additive. When the cathode comprises the conductive additive, it may be in a non-lithiated form present in the cathode where the cathode starts with sulfur (instead of Li_2S as the starting cathode or precursor), paired with lithium metal as the starting anode. Further, the present disclosure includes methods of forming an anode *in situ* in a battery system by providing the cathode and the cathode additive and activating the system to form the anode, supply the lithium and delithiate to form the conductive additive. The present battery cell system may be a high energy density battery.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] Figure 1. schematically demonstrates the concept cell reactions of Example 1, an anodeless lithium-sulfur cell with multi functional cathode additive (metal sulfide cathode additive).

[0021] Figure 2 schematically demonstrates the concept cell reactions of Example 2, an anodeless lithium-sulfur cell with multi functional cathode additive (metal sulfide cathode additive).

[0022] Figure 3 schematically demonstrates the concept cell reactions of Example 3, an anodeless lithium-sulfur cell with multi functional cathode additive (metal (Fe) sulfide cathode additive).

[0023] Figure 4 schematically demonstrates the concept cell reactions of Example 4, an anodeless lithium-sulfur cell with multi functional cathode additive (Ti sulfide cathode additive).

[0024] Figure 5 schematically demonstrates the concept cell reactions of Example 5, an anodeless lithium-sulfur cell with multi functional cathode additive (Cu sulfide cathode additive).

[0025] Figure 6 schematically demonstrates the concept cell reactions of Example 6, an anodeless lithium-ion cell with multi functional cathode additive (metal sulfide cathode additive).

[0026] Figure 7 schematically demonstrates the concept cell reactions of Example 7, an anodeless lithium-ion cell with multi functional cathode additive (metal sulfide cathode additive.

[0027] Figure 8 schematically shows in Fig. 8(a) lithium polysulfide and Fig. 8(b) high molecular weight lithium copper polysulfide.

[0028] Figure 9 shows a table of a theoretical energy density comparison of a Li-S electrochemical couple versus a Li-ion chemical system.

[0029] Figure 10 schematically shows a cathode additive system of the present disclosure in lithiated, non-lithiated and electrochemically active forms.

DETAILED DESCRIPTION

[0030] This disclosure provides embodiments of a cathode additive for use in anodeless cell systems or cell systems manufactured with anodes. The present cathode additive may supply the lithium in the cell system during cell activation. Use of the present cathode additive may reduce or eliminate the use of lithium metal in the cell manufacturing process. This in turn may help to maintain lower manufacturing or material costs while maintaining a high energy density advantage of the Li-S electrochemical couple. Lithium metal may no longer be needed in the electrode and cell assembly preparation because the use of the cathode additive may obviate the need to handle lithium metal during the process of manufacturing the cell.

[0031] In general, the cathode additives may be metallically conductive to at least partially replace the carbon additive; the cathode additive may be electrochemically active and may be discharged and cycled to provide capacity at the cell level; and, the present cathode additives may interact with polysulfide intermediates to reduce their solubility in the electrolyte, which may help the cycle life and reduce self-discharge. For example in Figure 10 it can be seen where both the lithiated cathode additive system and the non-lithiated cathode system are shown along with the cathode additive that is electrochemically active.

[0032] Other benefits may include improving cathode electronic conductivity and reducing the polysulfide dissolution in the electrolyte. Since the cathode additive may be uniformly distributed in the cathode, the cathode may also have improved and more uniform conductivity across the cathode matrix. Polysulfide anion dissolution in electrolyte may be an issue for Li-S chemical systems because capacity may be lost and there may be a high rate of self-discharge. Due to the uniform distribution of the present cathode (metal sulfide) additive inside the cathode, the interaction between the positively charged metal ion and the polysulfide anions may help to reduce the dissolution of these anions into the electrolyte, resulting in the improved cycle life and low self-discharge rate. The present cathode additive may modify the chemical structure of the polysulfide intermediates and reduce their solubility in the electrolyte (for example the non-aqueous electrolyte). Thus another benefit may be the formation of bivalent or multivalent metal polysulfide as Li-S cell charge/discharge intermediate. In addition to conductive metal sulfides, conductive metal polysulfides may also be formed during cell activation as a result of the presence of excess sulfur and lithium polysulfide intermediate.

[0033] Extra lithium may be introduced into the cell system without using lithium metal and while maintaining the high cathode utilization by applying multi functional cathode additives (metal sulfide cathode additives). The cathode additives may supply extra lithium sources into the cell system to compensate the lithium loss due to SEI layer formation. At the same time, the resulting product(s) of the cathode additive's oxidation (during cell activation) may act as a conductive additive to the cathode. Therefore, by using the cathode additives, the amount of the conventional cathode conductive additive, for example carbon black, carbon nanotubes or graphene, may be reduced or eliminated. In an exemplary Li-S system shown below in equation 1, for example, a cost reduction of about 35% by replacing $LiCoO_2$ as the cathode with Li_2S may be achieved. The exemplary Li-S system may also reduce or eliminate the inactive carbon black by about 15% when the cathode additive is delithiated and may act as a conductive additive.

[0034] Another possible benefit is the ability to maintain high cathode volumetric energy density, since the density of the multi functional cathode additives may be significantly higher than that of carbon black. In addition, the amount of desired extra lithium may also be adjusted by controlling the relative amount of cathode additive. The relative amount of extra lithium can be adjusted by changing the relative ratio between the additives as part of the cathode and the additives as part of the overall cell balance consideration. The extra lithium introduced in the cell system may therefore be controlled to be just enough to compensate for the loss of lithium during the irreversible first cycle . Thus, the cathode additive may make it possible to tune cell systems and offer a degree of flexibility for a wide variety of electrochemical cell couple systems.

Anodeless cell design

[0035] The present cathode additive may be used in an anodeless cell system design. The cathode additive may be multi-functional. The multi functional cathode additive in Figure 1 for example may be introduced into the cell system. After activation the cathode additive may provide extra lithium for long cycle life and when delithiated may act as the conductive additive to enable high cathode volumetric energy density and high cell discharge power.

[0036] An anodeless lithium cell design in the present disclosure can be defined as the following: lithium metal is not present on the anode current collector in a freshly built lithium rechargeable cell (see Figure 1). The freshly built lithium cell has a cathode, the cathode may be a sulfur cathode that is lithiated. A lithium metal anode may be induced *in situ* on the anode current collector by activating the cell during the first cell conditioning. Lithium may be supplied by a sulfur cathode of a freshly built cell. Since lithium metal (the anode active material) is not present on the anode current collector at the time the cell is built or constructed, it can be referred to as an anodeless cell design. This anodeless cell design may be applicable to other battery systems. This effectively may reduce or eliminate the anode preparation (coating, lamination or pressing) process step and reduce the cost associated with manufacturing environmental control and material handling. Examples of other anodeless rechargeable lithium cell designs may be found in U.S. Patent Nos. 7,632,602 and 6,168,884.

[0037] A separator such as for example a polyolefin separator and an electrolyte, such as an organic based electrolyte may be incorporated with the anodeless cell system. The separator may be between the cathode and the anode current collector. The electrolyte may comprise a liquid, a solid, or a polymer gel-type electrolyte. Specific examples may include but are not limited to a non-aqueous liquid or a solid polymer electrolyte that contains a dissolved lithium salt. The electrolyte useful in the present anodeless cell system may include any electrolyte know in the art.

[0038] An embodiment of a lithium battery utilizing the present cathode additive may include: an *in situ* electrochemically formed electrode comprising a conducting metal sulfide containing cathode and a lithium metal anode. Other components of the lithium battery may include a separator, a nonaqueous electrolyte solution, an external encapsulating shell, a cathode terminal, and an anode terminal. The *in situ* electrochemically formed electrode, the separator, and the nonaqueous electrolyte solution are encapsulated in the encapsulating shell. The *in situ* electrochemically formed electrode may be stacked and may sandwich the separator. The *in situ* electrochemically formed electrode can be in contact with or spaced from the separator. The cathode terminal is electrically connected with the cathode. The anode terminal is electrically connected with the anode.

[0039] In another embodiment hereof, a method of making the present lithium battery with an *in situ* electrochemically formed electrode is provided. The process may include: a) cathode preparation by using the conventional lithium-ion or other cathode preparation method, including coating a cathode mixture slurry on a current collector or pressing a cathode mixture onto the current collector, where the cathode mixture contains cathode precursor material, the multi functional additives, the conductive additive (may be present in a lower amount than what would be used without the present cathode additive), and binder materials; b) preparation of the anode by processing/cutting the anode current collector into the pre-determined shape and dimension without lithium metal; c) cell assembly by sandwiching separator material between the above prepared cathode and the anode current collector in multiple designs, such as cylindrical wound cell, prismatic wound cell, single cell stack layer or multiple plates cell stack designs; d) placement of the cell assembly inside a cell enclosure (case, pouch, etc.); e) activating the cell with electrolyte injection (for liquid electrolyte cell design) and sealing the enclosure; f) activating the cell by charging the cell to deposit lithium metal on the anode current collector surface and form the delithiated cathode material on the cathode while at the same time forming the conductive metal sulfide additive within the activated cathode.

Cell Activation

[0040] Both anode active material (Li metal) and cathode active material (sulfur) may be formed by cell activation using for example, Li_2S as the cathode precursor or cathode additive. An example of a lithium-sulfur cell (Li-S) system is shown in equation 1 where Li_2S is used as the cathode precursor material or cathode additive prior to cell activation. Li_2S replaces $LiCoO_2$ as the cathode material and acts as the precursor for cell activation. This may also increase the cathode volumetric energy density. The material for the cathode can be those know to one skilled in the art.

[0041] During activation, electrons may flow from the cathode side to the anode side through an external circuit. In the case of a Li-S system, Li_2S may be oxidized to form sulfur on the cathode and lithium ion may migrate from the cathode side through the electrolyte to the anode side. Being reduced in this manner may result in lithium metal deposition on the anode current collector. In addition, part of the lithium deposited on the anode current collector may be consumed by reacting with electrolyte to form a SEI protective layer. When the cells are discharged, the reverse reaction from equation 1 may deliver the cell energy to the targeted working loads, such as an electric vehicle, or other electronic devices.

$$Li_2S\text{ (Cathode) }\text{---}\!\!\rightarrow\text{ Li (anode) + S (Cathode)} \qquad (1)$$

[0042] An example of a possible activation reaction is shown in Figure 1. For cell activation, part of the lithium formed on the anode may react with electrolyte to form the SEI. The extra lithium formed from additive activation may compensate for the lithium loss.

Anode Containing Cell Systems

[0043] The present cathode additive in an anode containing cell system may provide a low cost Li-S battery technology with high energy density and power capability that may be delivered as a power source for Plug-in Electric Vehicle (PEV) applications. In addition to its use in the anodeless Li-S battery, the multi functional cathode additive can be integrated into other lithium battery and Li-ion (anode containing) battery chemical systems. The anode can be for example silicon, graphite, carbon, graphene, combinations thereof, or any material known to be used for the anode. The carbon may be in the form of for example a nanotube. The anode when supplied with lithium thus may comprise lithium metal, lithiated graphite, or lithium-Si alloy. Thus the present cathode additive may be used in a lithium-sulfur secondary battery with the cathode having the cathode additive as defined below as the conductive additive, along with an anode that has an alternative supply of lithium, a separator between the cathode and the anode, and an electrolyte. In such a case the cathode additive may function as the conductive additive and in reducing polysulfide dissolution in the electrolyte.

[0044] Additional components such as electrolytes, terminals, casings and other components known in the art can be combined with the lithium battery containing the cathode additive described herein to produce operable lithium batteries for powering electrical devices. The cell system may be in the form of a thin-film, thick-film or bulk battery. These systems may include high energy density batteries, secondary batteries or rechargeable batteries such as for example, Li batteries such as Li-S or Na-S, or Li-ion batteries. It is desirable to use the present cathode additive in batteries for a variety of devices such as for example, complementary metal oxide semiconductor (CMOS) back-up power, microsensors, smart cards, radio frequency identification (RFID) devices, and micro-actuators. Other devices may include personal digital assistants, and portable electronics.

Cathode Additive

[0045] The present cathode additive may contain Li such as for example in the form of a lithiated metal sulfide having the formulae $Li_{2-x}MS$, $Li_{2-x}MS_2$, or $Li_{2-x}MS_n$ where $0<x<2$ is , n is equal to or larger than 1, and M is a transition metal. The cathode additive may be either a single compound, such as $LiTiS_2$, $LiCuS$, Li_2FeS_2, $LiCoS_2$, $LiCuS_2$, or a mixture of the chemicals, such as Li_2S/Cu_2S and Li_2S/Fe (or equivalent chemical composition such as for example, $Li_2S + Cu_2S$ is the equivalent of $2LiCuS$). The particle size of the present cathode additive may vary depending on the material used as the cathode additive. The particle size of the cathode additive may be in the range of nanometer to micrometer size. The smaller the particle size of the cathode additive, the easier or faster and more efficient the electrochemical reaction may be.

[0046] With the present cathode additive utilized in a lithium battery, upon cell activation, the metal sulfide additive may provide more lithium to the anode and at the same time the resulting delithiation product(s) may act as a conductive additive to boost the cathode electronic conductivity that may contribute to replacing the carbon additive, at least partially, for improved volumetric cathode energy density. Examples of conductive cathode additives after cell activation may include but are not limited to: CoS_2, CuS_2, CuS, TiS_2, FeS, $Fe_{2-x}S$ (where x is smaller than 2), Fe_7S_8, NiS_2, MnS_2, MoS_2, or FeS_2. These conductive metal sulfides can be formed *in situ* during the anodeless Li-S cell activation. The metallic (electric) conductivity of the *in situ* electrochemically formed metal sulfides may vary.

[0047] The multi functional cathode additive may be defined as any compound or combination of compounds that contain lithium as part of their chemical composition, and such compounds in a cell system may provide or be regulated to provide more lithium to the anode, may result in the formation of electronic conductive product(s) upon oxidation (same as cell activation – cathode oxidation), may reduce polysulfide dissolution in the electrolyte, or any combination thereof. During the oxidation reaction, lithium ion may be released from the chemical composition, which may be deposited on the anode in an electrochemical cell system. As the compound may be delithiated, it may result in the formation of the conductive additive. And, the compound may reduce polysulfide dissolution in the electrolyte of the cell system.

[0048] When applied to Li-ion systems, the system may have for example, lithium alloy or lithium intercalation anodes. The extra Li introduced by the cathode additive may be sufficient to compensate for the Li loss during SEI formation, or sufficient such that the excess Li metal at the anode does not destabilize the cell. When used with a Li alloy or Li intercalation compound anode, the cathode additive may perform the functions already described when the amount of excess Li in the initial cathode material is chosen to compensate for the Li loss during SEI formation without the need for Li metal at the anode.

[0049] Due to the conducting nature of the cathode additive when it is delithiated, the amount of filler (e.g., carbon black, carbon nanotubes, or graphene) generally used to improve cathode conductivity may be reduced, which may in turn improve the volumetric energy density of the cathode due to the density difference between the metal sulfide and other filler materials. The non-lithiated cathode additive may also act as a high rate cathode under high pulse current discharge conditions. This may improve the pulse power capability of Li-S batteries for PEV applications.

[0050] The redox couple in a Li-S battery, namely both sulfur and Li_2S, is electronically insulating. Therefore, carbon black or other non-active carbon materials may be added to the cathode formulation as a conductive additive to increase its electronic conductivity. However, this may result in reduced sulfur cathode gravimetric and volumetric energy densities since the conductive additives added to the cathode formulation are not electrochemically active (i.e., electrochemically non-active).

[0051] In certain embodiments, before cell activation the cathode additive compound can be either electrically conductive or electrically non-conductive. However, the *in situ* formed delithiated metal sulfide species derived from the cathode additive during the anodeless cell activation may be electronically conductive to act as a conductive additive. A possible activation reaction is shown in Figure 1. The anodeless cell in Figure 1 includes the anode current collector, the electrolyte (solid or liquid), a separator layer, a cathode containing Li_2S + Fe, and the cathode current collector. After charging and activating the cell, a Li metal layer is formed between the anode current collector and the electrolyte, with a separator layer and activated cathode, S + FeS_2. With cycles of charging and discharging after activation, the cathode cycles between S + FeS_2 and Li_2S + FeS_2.

[0052] The resulting conductive additive after cell activation may be for example MS or MS_2 and may include, but are not limited to, CoS_2, Cu_2S, CuS, CuS_2, TiS_2, FeS_2, FeS, $Fe_{2-x}S$ (where x is smaller than 2), NiS_2, MnS_2, MoS_2, Fe_7S_8, or metal polysulfides (MS_n) where $2 < n < 8$) and M may be Co, Cu, Ni, Mn, Mo, Ti, Fe, or the like, or $Li_{2-x}MS$, or $Li_{2-x}MS_2$ or $Li_{2-x}MS_n$ where ($0<x<2$), n is equal to or greater than 1, and M may be Co, Cu, Ni, Mn, Mo, Ti, Fe, or the like. The cathode additive metal cation may have a multi-valence. The molecular weight of the polysulfide intermediates may be effectively doubled or tripled as illustrated in Figure 8 using Cu(II) and S_6^{2}- as an example. The metal polysulfide interaction may also yield a cyclic structure. The metal polysulfide intermediates with high molecular weight may result in lower electrolyte dissolution than lithium polysulfide. See Figures 8(a) and 8(b).

[0053] In certain embodiments, the cell activation charge capacity is equal to the capacity of the cell cathode, such as Li_2S (1167 mAh/g), plus the capacity of the multi functional cathode additive, such as $LiTiS_2$ (225 mAh/g).

[0054] In certain embodiments, the voltage difference between the cathode and the conductive additives is at least 0.0V or larger (i.e., is positive) with cathode electrochemical potential (or voltage) equal to or higher than the additive electrochemical potential (or voltage).

[0055] Embodiments of the cathode additive also include its use in a lithium-sulfur secondary battery which includes the cathode having the cathode additive as defined above, an electrically conductive material, and a binder. In such a case the cathode additive may function as a source of lithium and in reducing polysulfide dissolution in the electrolyte.

[0056] Embodiments further include a method of making a cell system with the present cathode additive. The method includes: mechanical mixing, ball milling, and chemically or electrochemically synthesizing lithiated metal sulfides. The lithium battery can be made in various sizes. During the manufacture of an electrochemical device, the solid electrolyte layer may be deposited with a cathode.

[0057] Careful selection of cathode additives capable of forming conductive additives may provide high cell pulse power under high current density pulse discharge conditions. Electrode power capability may be controlled in several ways. The first is the inherent electronic conductivity of the electrode active materials. The second is the selection of conductive additives and binders. And the third is the electrode formulation and ionic conductivity.

EXAMPLES

[0058] Li-S cell system is used as an electrochemical cell vehicle in the following examples to demonstrate the dual functional cathode additive concept in an anodeless cell design.

[0059] Example 1:

Cell Activation: $Li_2S \dashrightarrow 2Li$ (Anode) + S (Cathode)

Initial Additive Activation: $Li_2S + Fe \dashrightarrow 2Li$ (Extra) + FeS (Conductive)

General Additive Activation: $Li_2S + M \dashrightarrow 2Li$ (Extra) + MS (Conductive)

[0060] Figure 1 schematically demonstrates the concept cell reactions of Example 1.

[0061] Example 2:

Cell Activation: $Li_2S \dashrightarrow 2Li$ (Anode) + S (Cathode)

Initial Additive Activation: $2Li_2S + Fe \dashrightarrow 4Li$ (Extra) + FeS_2 (Conductive)

General Additive Activation: $2Li_2S + M \dashrightarrow 4Li$ (Extra) + MS_2 (Conductive)

[0062] Figure 2 schematically demonstrates the concept cell reactions of Example 2.

[0063] Example 3:

Cell Activation: $Li_2S \dashrightarrow 2Li$ (Anode) + S (Cathode)

Initial Additive Activation: $Li_2FeS_2 \dashrightarrow 2Li$ (Extra) + FeS_2 (Conductive)

General Additive Activation: $Li_2MS_2 \dashrightarrow 2Li$ (Extra) + MS_2 (Conductive)

[0064] Figure 3 schematically demonstrates the concept cell reactions of Example 3.

[0065] Example 4:

Cell Activation: Li_2S ---→ 2Li (Anode) + S (Cathode)

Initial Additive Activation: $LiTiS_2$ ---→ Li (Extra) + TiS_2 (Conductive)

General Additive Activation: LiMS2 ---□ Li (Extra) + MS2 (Conductive)

[0066] Figure 4 schematically demonstrates the concept cell reactions of Example 4.

[0067] Example 5:

Cell Activation: Li_2S ---→ 2Li (Anode) + S (Cathode)

Initial Additive Activation: Li_2S + Cu_2S ---→ 2Li (Extra) + 2CuS (Conductive)

General Additive Activation: Li_2S + M_2S ---→ 2Li (Extra) + 2MS (Conductive)

[0068] Figure 5 schematically demonstrates the concept cell reactions of Example 5.

[0069] The above examples provide several possible pathways for extra lithium formation and conductive sulfide formation. The additive activation equation where M represents any metal element that forms electronically conductive sulfide compound such as for example Fe, Co, Ni, Ti, Mn, Mo, or the like. Other variables are possible, such as metal polysulfide MS_x ($x > 2$) or partially lithiated metal sulfide, such as $Li_{2-x}MS_2$ (where $0<x<2$). In addition, the resulting conductive sulfide compound could also contain multiple metals ($M^1M^2S_x$ ($x \geq 2$), such as $CuFeS_2$.

[0070] It should be noted that metal sulfide materials have been widely used as cathode material in the thermal batteries and has been studied at room temperature for rechargeable system. Their reversible charge/discharge capability at room temperature has been demonstrated in the literature – an example is shown in the following equation (2):

$$TiS_2 + Li \underset{Charge}{\overset{Discharge}{\rightleftharpoons}} LiTiS_2 \qquad (2)$$

[0071] Therefore, to maintain the cathode additive in the MS_2 (or MS) structure, after activation, the cell discharge voltage limit may be controlled to be higher than the discharge running voltage of MS_2 material. Another advantage of the present battery system is that the *in situ* formed cathode additive of metal sulfide itself is cathode material and has high power capability as demonstrated in thermal batteries (> 100 mA/cm^2 high rate discharge capability). Thus with the proposed chemical systems, cell high pulse power capability may be achieved over the system without the additives under the condition that the cell voltage polarized under high current density pulses discharge to the electrochemical potentials below the discharge running voltage of the metal sulfide additive.

[0072] Beyond Lithium metal anode cell system, the concept can also be used in Li-ion cell systems. The following examples demonstrate the possible benefit of this concept to other high voltage Li-ion chemical systems, including the ones with lithium intercalation anode and lithium alloy anode.

[0073] Example 6:

Cell Activation: $LiFePO_4 + 6C \dashrightarrow LiC_6$ (Anode) + $FePO_4$ (Cathode)

Initial Additive Activation: $LiTiS_2 + 6C \dashrightarrow LiC_6$ (Extra) + TiS_2 (Conductive)

General Additive Activation: $LiMS_2 + 6C \dashrightarrow LiC_6$ (Extra) + MS_2 (Conductive)

[0074] Figure 6 schematically demonstrates the concept cell reactions of Example 6.

[0075] Example 7:

Cell Activation: $44LiCoO_2 + 5Si \dashrightarrow Li_{22}Si_5$ (Anode) + $44Li_{0.5}CoO_2$ (Cathode)

Initial Additive Activation: $22LiTiS_2 + 5Si \dashrightarrow Li_{22}Si_5$ (Extra) + $22TiS_2$ (Conductive)

General Additive Activation: $22LiMS_2 + 5Si \dashrightarrow Li_{22}Si_5$ (Extra) + $22MS_2$ (Conductive)

[0076] Figure 7 schematically demonstrates the concept cell reactions of Example 7.

[0077] The description has not attempted to exhaustively enumerate all possible variations. The alternate embodiments may not have been presented for a specific portion of the invention, and may result from a different combination of described portions, or that other undescribed alternate embodiments may be available for a portion, is not to be considered a disclaimer of those alternate embodiments. It will be appreciated that many of those undescribed embodiments are within the literal scope of the following claims, and others are equivalent. Furthermore, all references, publications, U.S. Patents, and U.S. Patent Application Publications cited throughout this specification are incorporated by reference as if fully set forth in this specification.

CLAIMS:

1. A battery cell system comprising

(a) a cathode,

(b) an anode current collector,

(c) a separator between said cathode and said anode current collector, and

(d) an electrolyte.

wherein said cathode comprises a cathode additive, and wherein said cathode additive is a lithium containing compound and is delithiated to supply lithium to form an anode *in situ*.

2. The battery cell system of claim 1 wherein further said cathode additive forms a conductive additive when said cathode additive is delithiated.

3. The battery cell system according to claim 1 wherein the delithiated cathode additive forms a conductive additive of a metal sulfide (MS), or a metal polysulfide (MS_n) where n is larger than 1, and M is a transition metal,

4. The battery cell system according to claim 1 wherein the cathode additive is a lithium metal sulfide (Li_{2-x} MS, $Li_{2-x}MS_2$, or Li_{2-x} MS_n) where $0<x<2$, n is equal to or larger than 1, and M is a transition metal.

5. The battery cell system of claim 1 wherein the delithiated cathode additive forms a conductive additive of a metal sulfide (MS) where M is Co, Cu, Ni, Mn, Mo, Ti, or Fe.

6. The battery cell system of claim 1 wherein the delithiated cathode additive forms a conductive additive of a metal polysulfide selected from the group consisting of CoS_2, Cu_2S, CuS, CuS_2, TiS_2, FeS_2, FeS, $Fe_{1-x}S$ (where x is less than 1), NiS_2, MnS_2, MoS_2, and Fe_7S_8.

7. The battery cell system of claim 1 wherein the cathode is a lithiated sulfur cathode.

8. The battery cell system of claim 1 wherein said cathode additive supplies lithium to the anode current collector to form the anode.

9. A battery cell system comprising

(a) a cathode,

(b) an anode,

(c) a separator between said cathode and said anode, and

(d) an electrolyte,

wherein said cathode comprises a cathode additive or a conductive additive.

10. The battery cell system according to claim 9 wherein said conductive additive is selected from the group consisting of metal sulfide (MS), a metal polysulfide (MS_n) where n is larger than 1, and M is a transition metal.

11. The battery cell system of claim 9 wherein said conductive additive is a transition metal sulfide.

12. The battery cell system of claim 9 wherein said cathode is a sulfur material and said conductive additive is a metal sulfide (MS) where M is Co, Cu, Ni, Mn, Mo, Ti, or Fe.

13. The battery cell system of claim 9 wherein said cathode is a sulfur material and the conductive cathode additive is a metal polysulfide selected from the group consisting of CoS_2, Cu_2S, CuS, CuS_2, TiS_2, FeS_2, FeS, $Fe_{1-x}S$ (where x is less than 1), NiS_2, MnS_2, MoS_2, and Fe_7S_8.

14. The battery cell system of claim 9 wherein said cathode is a sulfur cathode.

15. The battery cell system according to claim 9 wherein said cathode additive is a lithium containing compound.

16. The battery cell system according to claim 9 wherein said cathode additive is a lithium metal sulfide ($Li_{2-x}MS$, $Li_{2-x}MS_2$ or $Li_{2-x}MS_n$) where ($0<x<2$), n is equal to or larger than 1, and M is a transition metal.

17. The battery cell system according to claim 9 wherein said cathode additive is a lithium metal sulfide selected from the group consisting of $LiTiS_2$, Li_2FeS_2, Li_2S/Cu_2S, Li_2S/Cu, and Li_2S/Fe, Li_2S/FeS, Li_2S/Co, Li_2S/CoS.

18. The battery cell system of claim 9 wherein the cathode additive is delithiated to form a metal polysulfide selected from the group consisting of CoS_2, Cu_2S, CuS, CuS_2, TiS_2, FeS_2, FeS, $Fe_{1-x}S$ (where x is less than 1), NiS_2, MnS_2, MoS_2, and Fe_7S_8.

19. The battery cell system according to claim 9 wherein said cathode is a sulfur cathode or a lithiated sulfur cathode.

20. The battery cell system according to claim 9 further comprising a cathode precursor of Li_2S.

21. The battery cell system according to claim 9 wherein said cathode additive supplies lithium to the anode.

22. A method of forming an anode *in situ* in a battery cell system, said method comprising

providing a cathode,

providing a cathode additive, and

activating the battery cell system to form upon activation the anode, supply lithium to the battery cell system, and delithiate the cathode additive to form a conductive additive.

23. The method of claim 19 wherein the supplying lithium comprises supplying lithium to the anode formed *in situ*.

24. A lithium battery comprising a cathode, an anode, and a cathode additive that provides excess lithium to the anode, is conductive after delithiation, and reduces polysulfide dissolution in the electrolyte.

25. A high energy density battery comprising a cathode, wherein the cathode comprises a cathode additive, an anode current collector, a separator between said cathode and said anode current collector, and an electrolyte, and wherein an anode is formed *in situ* after activation of the high energy density battery.

Fig. 1

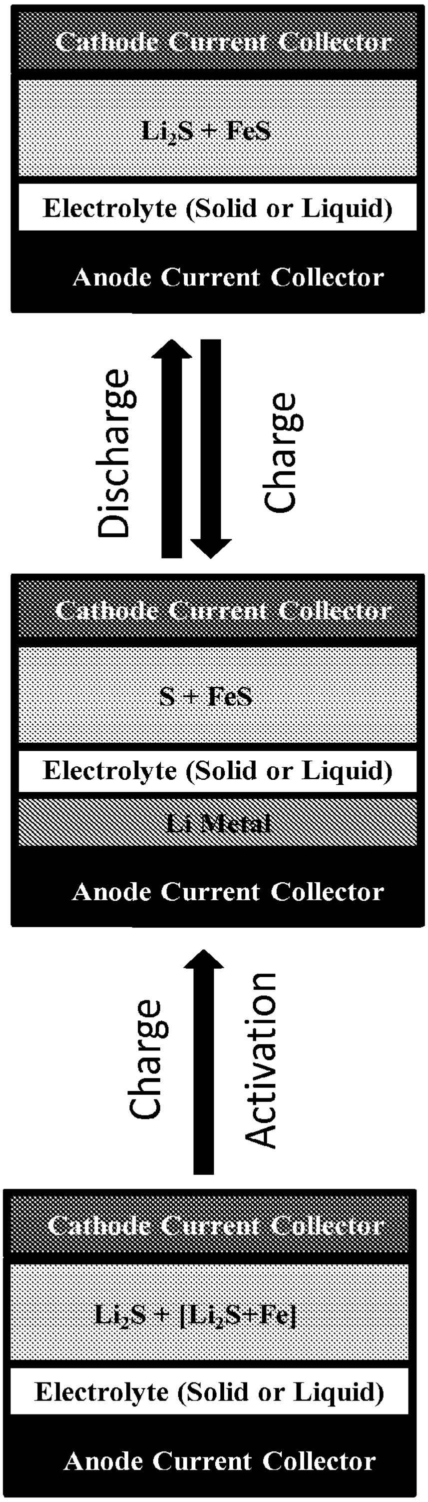
Cathode Current Collector
Li_2S + FeS
Electrolyte (Solid or Liquid)
Anode Current Collector
Discharge
Charge
Cathode Current Collector
S + FeS
Electrolyte (Solid or Liquid)
Li Metal
Anode Current Collector
Charge
Activation
Cathode Current Collector
Li_2S + [Li_2S+Fe]
Electrolyte (Solid or Liquid)
Anode Current Collector

Fig. 2

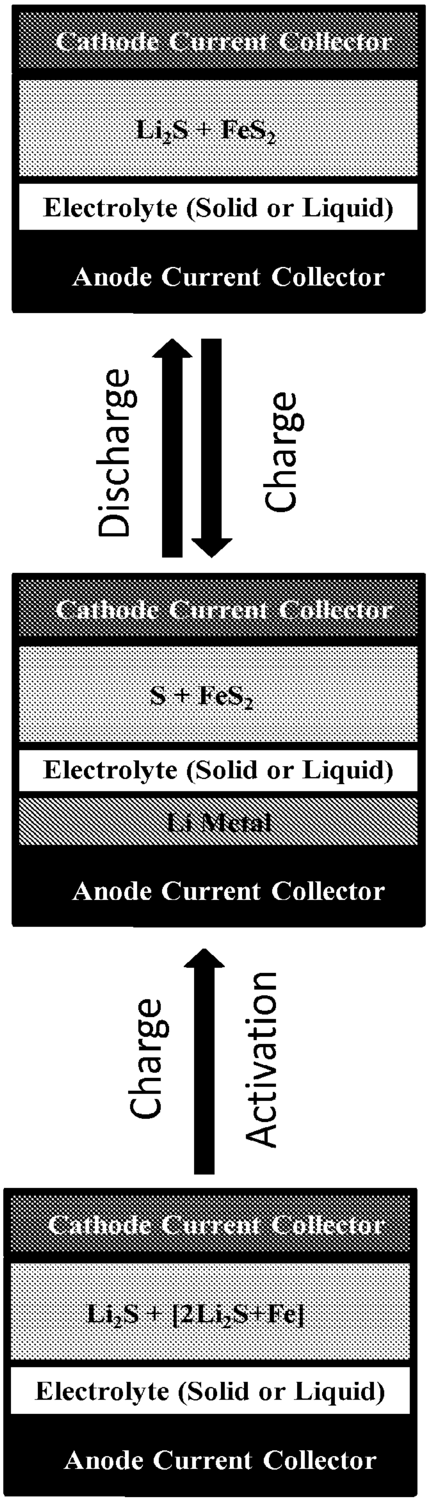
Cathode Current Collector
$Li_2S + FeS_2$
Electrolyte (Solid or Liquid)
Anode Current Collector
Discharge
Charge
Cathode Current Collector
$S + FeS_2$
Electrolyte (Solid or Liquid)
Li Metal
Anode Current Collector
Charge
Activation
Cathode Current Collector
$Li_2S + [2Li_2S+Fe]$
Electrolyte (Solid or Liquid)
Anode Current Collector

Fig. 3

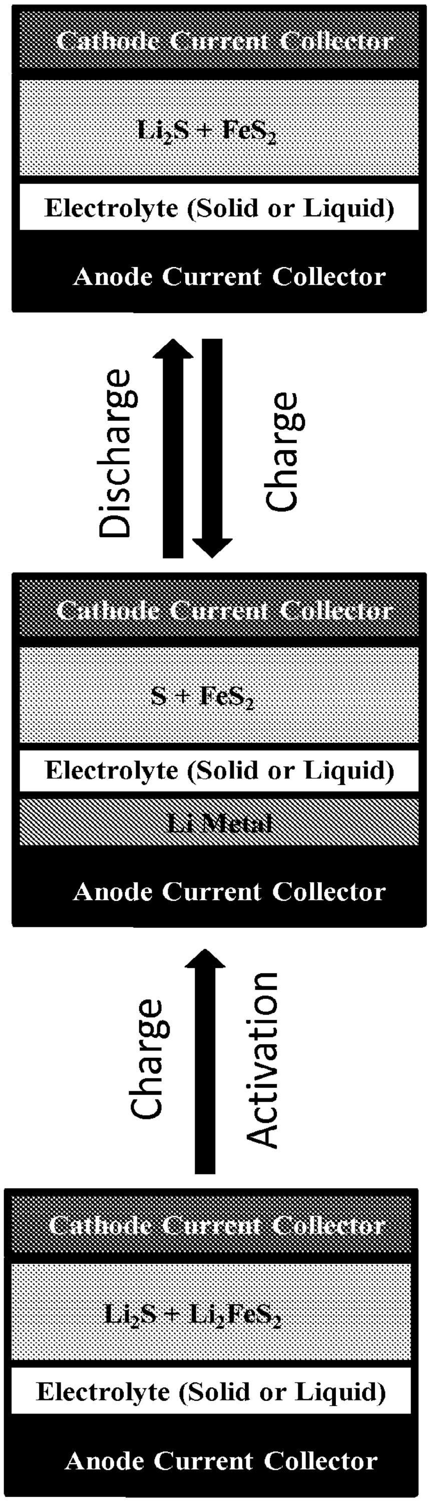
Cathode Current Collector
$Li_2S + FeS_2$
Electrolyte (Solid or Liquid)
Anode Current Collector
Discharge
Charge
Cathode Current Collector
$S + FeS_2$
Electrolyte (Solid or Liquid)
Li Metal
Anode Current Collector
Charge
Activation
Cathode Current Collector
$Li_2S + Li_2FeS_2$
Electrolyte (Solid or Liquid)
Anode Current Collector

Fig. 4

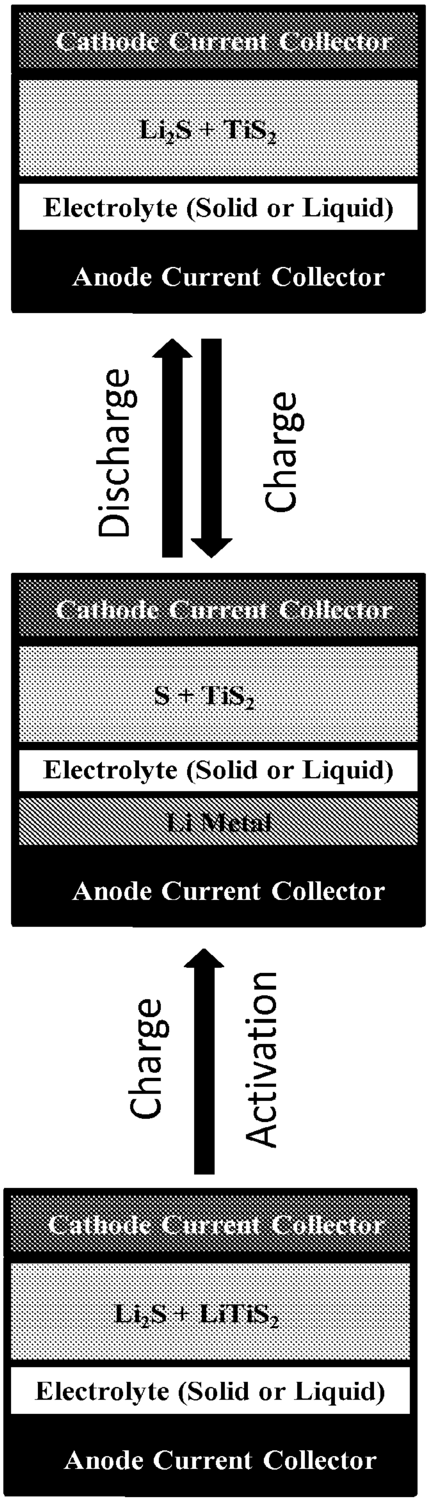
Cathode Current Collector
$Li_2S + TiS_2$
Electrolyte (Solid or Liquid)
Anode Current Collector
Discharge
Charge
Cathode Current Collector
$S + TiS_2$
Electrolyte (Solid or Liquid)
Li Metal
Anode Current Collector
Charge
Activation
Cathode Current Collector
$Li_2S + LiTiS_2$
Electrolyte (Solid or Liquid)
Anode Current Collector

Fig. 5

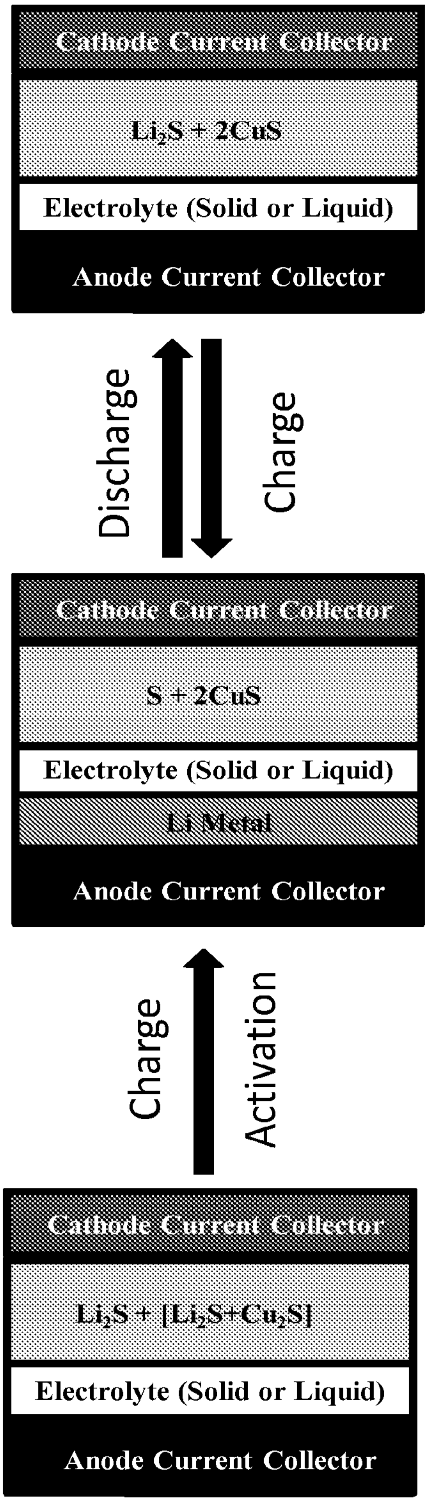
Cathode Current Collector
$Li_2S + 2CuS$
Electrolyte (Solid or Liquid)
Anode Current Collector
Discharge
Charge
Cathode Current Collector
$S + 2CuS$
Electrolyte (Solid or Liquid)
Li Metal
Anode Current Collector
Charge
Activation
Cathode Current Collector
$Li_2S + [Li_2S+Cu_2S]$
Electrolyte (Solid or Liquid)
Anode Current Collector

Fig. 6

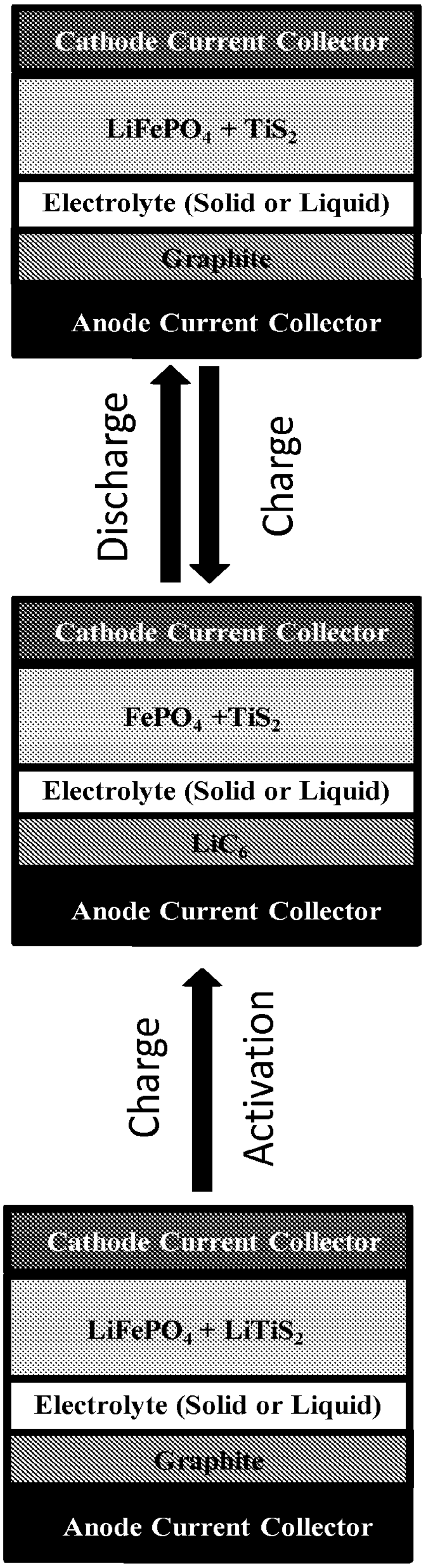
Cathode Current Collector
LiFePO4 + TiS2
Electrolyte (Solid or Liquid)
Graphite
Anode Current Collector
Discharge
Charge
Cathode Current Collector
FePO4 +TiS2
Electrolyte (Solid or Liquid)
LiC6
Anode Current Collector
Charge
Activation
Cathode Current Collector
LiFePO4 + LiTiS2
Electrolyte (Solid or Liquid)
Graphite
Anode Current Collector

Fig. 7

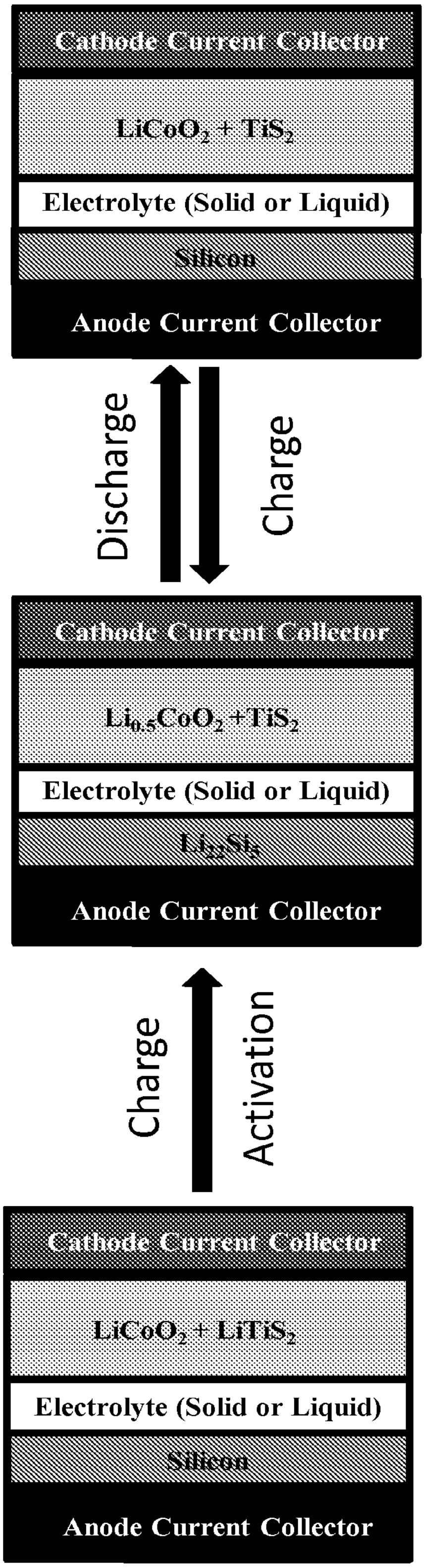
Cathode Current Collector
$LiCoO_2 + TiS_2$
Electrolyte (Solid or Liquid)
Silicon
Anode Current Collector
Discharge
Charge
Cathode Current Collector
$Li_{0.5}CoO_2 + TiS_2$
Electrolyte (Solid or Liquid)
$Li_{22}Si_5$
Anode Current Collector
Charge
Activation
Cathode Current Collector
$LiCoO_2 + LiTiS_2$
Electrolyte (Solid or Liquid)
Silicon
Anode Current Collector

Fig. 8

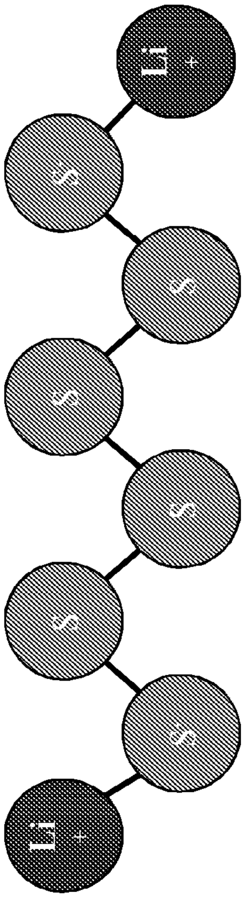

Fig. 8(a): Li_2S_6 MW = 206.3

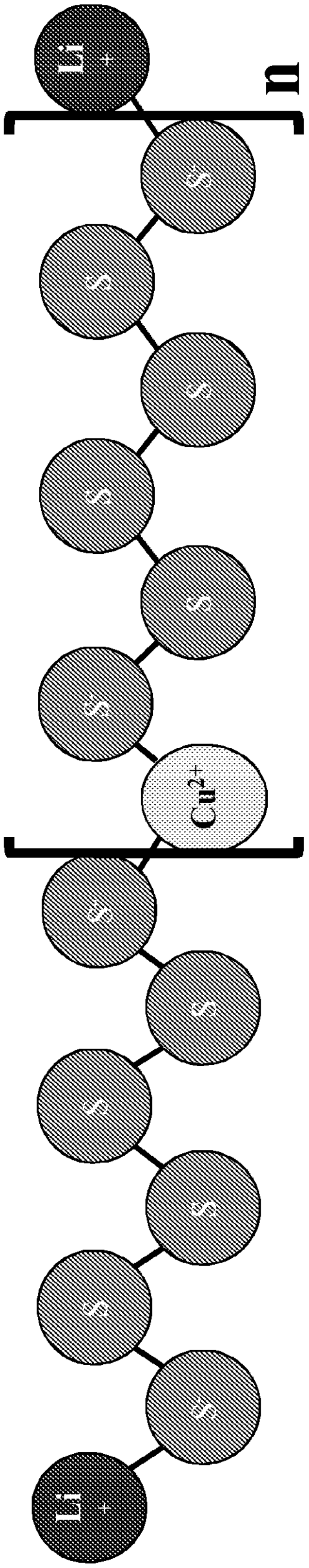

Fig. 8(b): $Li_2Cu_nS_{6n+6}$ MW = 462.2 (n = 1); 718.2 (n = 2)

Fig. 9

Electrode Material	Cell Voltage	Theoretical Capacity Density		Theoretical Energy Density of the Couple	
	V	Ah/kg	Ah/L	Wh/kg*	Wh/L**
LiCoO2/Graphite	3.9	372	761	390	1391
		137	671		
Sulfur/Li Metal	2.1	3862	2062	2450	2678
		1672	3343		
Anodeless -Li_2S/Li	2.1	3862	2062	2450	4066
		1167	1936		

* Active material only, assuming with theoretical cell balance

** Active material only, assuming with theoretical cell balance; calculated using true material density

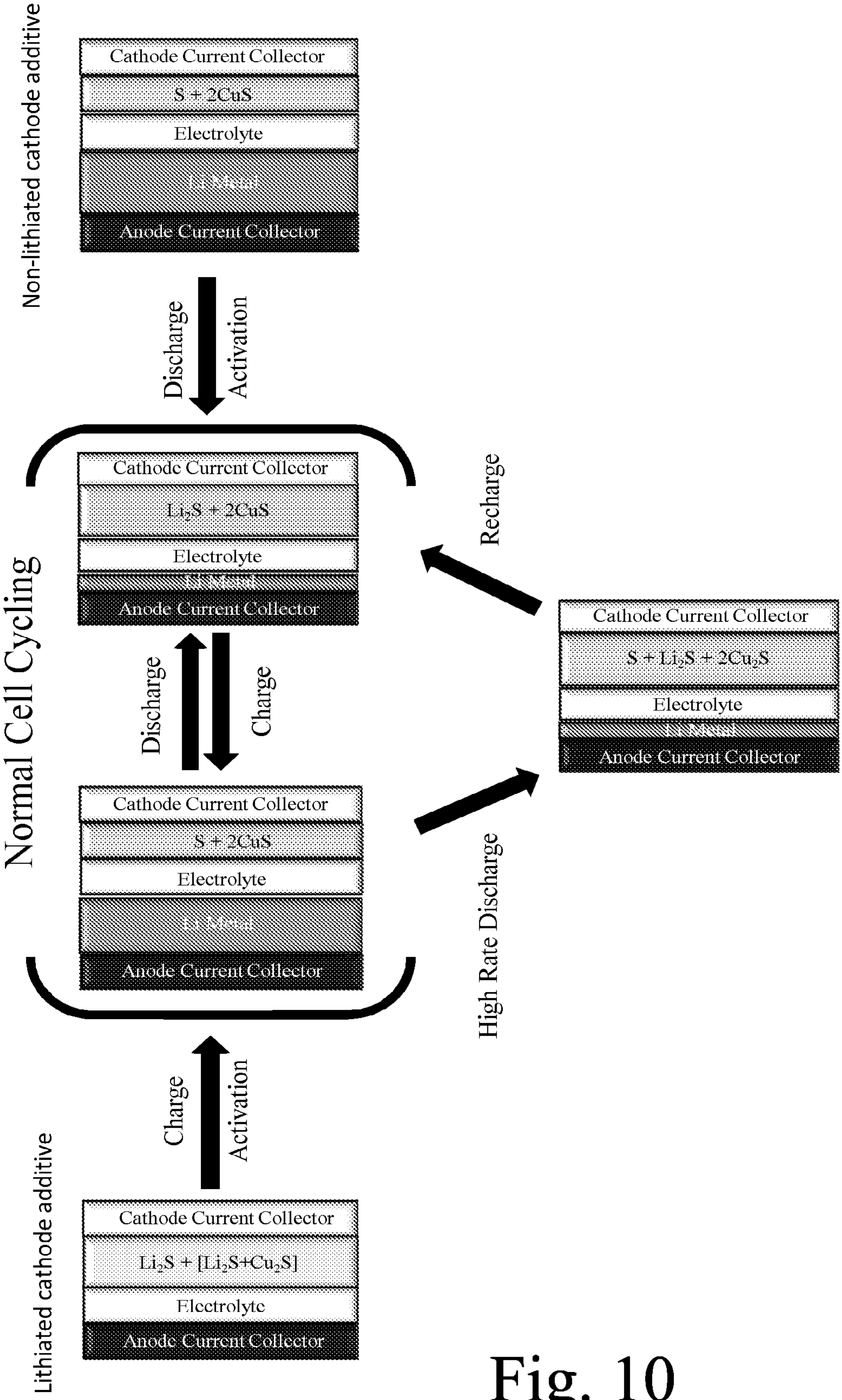
Non-lithiated cathode additive
Cathode Current Collector
$S + 2CuS$
Electrolyte
Li Metal
Anode Current Collector
Discharge
Activation
Normal Cell Cycling
Cathode Current Collector
$Li_2S + 2CuS$
Electrolyte
Li Metal
Anode Current Collector
Recharge
Cathode Current Collector
$S + Li_2S + 2Cu_2S$
Electrolyte
Li Metal
Anode Current Collector
Discharge
Charge
High Rate Discharge
Cathode Current Collector
$S + 2CuS$
Electrolyte
Li Metal
Anode Current Collector
Charge
Activation
Lithiated cathode additive
Cathode Current Collector
$Li_2S + [Li_2S+Cu_2S]$
Electrolyte
Anode Current Collector

Fig. 10

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2015/016363

A. CLASSIFICATION OF SUBJECT MATTER

H01M 10/052 *(2010.01)*
H01M 4/58 *(2010.01)*

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01M 10/00, 10/056, 10/052, 4/00, 4/62, 4/58, 4/48, 4/36, 4/02

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)

PatSearch (RUPTO internal), USPTO, PAJ, Esp@cenet, DWPI, EAPATIS, PATENTSCOPE, Information Retrieval System of FIPS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2006/100464 A2 (OXIS ENERGY LIMITED et al.) 28.09.2006, p. 3, lines 28-30, p. 4, line 20, p. 6, lines 22-23, 30-p. 7, line 10, p. 10, lines 8-15, p. 12, lines 2-6, claims 1, 12	1, 2, 7-9, 15, 19-25
Y		3, 5, 6, 10-14, 18
A		4, 16, 17
Y	US 2004/0101753 A1 (DUCK-CHUL HWANG) 27.05.2004, claims 1-4, 29	3, 5, 6, 10-14, 18
A	EP 1815546 A1 (OXIS ENERGY LIMITED) 08.08.2007, claims	1-25
A	US 2007/0015055 A1 (JAE HYUN LEE et al.) 18.01.2007, claims	1-25
A	US 5814420 A (POLYPLUS BATTERY COMPANY, INC.) 29.09.1998, claims	1-25

☐ 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	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier document but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 06 May 2015 (06.05.2015)	Date of mailing of the international search report 04 June 2015 (04.06.2015)
Name and mailing address of the ISA/RU: Federal Institute of Industrial Property, Berezhkovskaya nab., 30-1, Moscow, G-59, GSP-3, Russia, 125993 Facsimile No: (8-495) 531-63-18, (8-499) 243-33-37	Authorized officer E. Kovaleva Telephone No. 499-240-25-91