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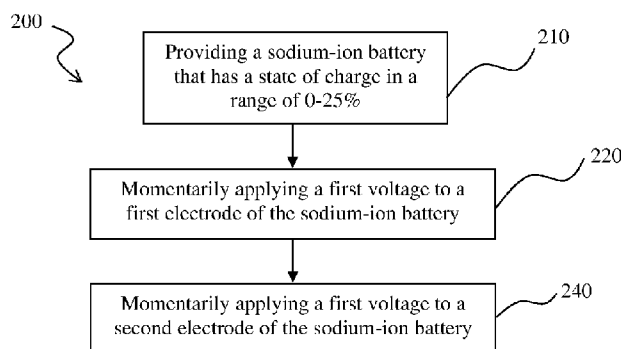


FIG. 2

(57) Abstract: A method of improving a sodium-ion battery, the method comprising: a) momentarily applying a first voltage to a first electrode of the sodium-ion battery having a state of charge in the range of 0-25%; and b) momentarily applying a second voltage to a second electrode of the sodium-ion battery. An improved sodium-ion battery comprising: a first electrode to which a first voltage has been momentarily applied when the sodium-ion battery has a state of charge in a range of 0-25%; and a second electrode to which a second voltage has been momentarily applied when the sodium-ion battery has a state of charge in the range of 0-25%.



METHOD OF IMPROVING A SODIUM-ION BATTERY AND AN IMPROVED SODIUM-ION BATTERY

TECHNICAL FIELD

[0001] This invention relates to a method of improving a sodium-ion battery and an improved sodium-ion battery.

BACKGROUND

[0002] Fossil fuels are falling out of favour due to environmental problems associated with their production and use. Consequently, the demand for electrically powered cars is increasing. At the same time, the demand for other mobile devices that are powered with electricity, such as smart phones, tablets and laptops, is also going up. In order to power electric cars and other mobile devices, portable sources of electrical energy are needed and it is desirable that they should provide the electrical energy for as long as possible in between charges.

[0003] Portable sources of electrical energy include lithium-ion batteries. While lithium-ion batteries are already in common use, they present a known fire hazard and are also environmentally damaging to produce. Sodium-ion batteries are being developed as a viable alternative to lithium-ion batteries that alleviate some, if not all, of the problems associated with lithium-ion batteries. However, currently available sodium-ion batteries are not yet able to achieve the energy density of existing lithium-ion batteries for batteries of the same size.

[0004] It is thus desirable to improve one or more of the overall capability, capacity, and life cycle of sodium-ion batteries in order for them to be able to meet today's energy demands.

SUMMARY

[0005] The present application discloses the empirical discovery of a method for improving a sodium-ion battery such that the energy capacity is significantly improved.

[0006] According to a first aspect, there is provided a method of improving a sodium-ion battery, the method comprising:

- a) momentarily applying a first voltage to a first electrode of the sodium-ion battery having a state of charge in a range of 0-25%; and
- b) momentarily applying a second voltage to a second electrode of the sodium-ion battery.

[0007] The method may further comprise, after step b), repeating step a).

[0008] The method may further comprise, after repeating step a), repeating step b).

[0009] According to some embodiments, the sodium-ion battery has a state of charge of 0%. For such a sodium-ion battery, momentarily applying the first voltage in step b) may be configured such that the sodium-ion battery remains uncharged after the first voltage has been momentarily applied.

[0010] According to some embodiments, the sodium-ion battery has a state of charge of 0%. For such a sodium-ion battery, momentarily applying the second voltage in step c) may be configured such that the sodium-ion battery remains uncharged after the second voltage has been momentarily applied.

[0011] The sodium-ion battery that has a state of charge of 0% may be a newly produced sodium-ion battery before it is first charged for use.

[0012] According to a second aspect, there is provided an improved sodium-ion battery comprising: a first electrode to which a first voltage has been momentarily applied when the sodium-ion battery has a state of charge in a range of 0-25%; and a second electrode to which a second voltage has been momentarily applied when the sodium-ion battery has a state of charge in a range of 0-25%.

[0013] In some embodiments, the sodium-ion battery may have a state of charge of 0% and remain uncharged after the first voltage had been momentarily applied.

[0014] In some embodiments, the sodium-ion battery may have a state of charge of 0% and remain uncharged after the second voltage has been momentarily applied.

[0015] The sodium-ion battery that has a state of charge of 0% may have been a newly produced sodium-ion battery before it was first charged for use.

[0016] For both aspects, the first voltage and the second voltage may each have one of: a DC rectangular wave form, a half sine wave form, and a combination of a DC rectangular wave form and a half sine wave form.

[0017] The first electrode may be a negative electrode of the sodium-ion battery when the sodium-ion battery is charged for use and the second electrode may be a positive electrode of the sodium-ion battery when the sodium-ion battery is charged for use.

[0018] The first voltage and the second voltage may each range from 0.5V to 300V.

[0019] Current during application of each of the first voltage and the second voltage may range from 0.1A to 1,000A.

[0020] A duration of application of the first voltage and duration of application of the second voltage may each range from 1/1000 seconds to 1/2 seconds.

BRIEF DESCRIPTION OF DRAWINGS

[0021] In order that the invention may be fully understood and readily put into practical effect there shall now be described by way of non-limitative example only exemplary embodiments of the present invention, the description being with reference to the accompanying illustrative drawings, in which:

FIG. 1 is a schematic illustration of an exemplary embodiment of a sodium-ion battery during discharge.

FIG. 2 a flowchart of an exemplary method of improving the sodium-ion battery of FIG. 1.

FIG. 3A is schematic illustrations of active particles or molecules on an electrode surface of the sodium-ion battery before performing the method of FIG. 2.

FIG. 3B is schematic illustrations of active particles or molecules on an electrode surface of the sodium-ion battery after performing the method of FIG. 2.

FIG. 4 shows exemplary electric wave forms of various voltages that may be applied to electrodes of the sodium-ion battery.

FIG. 5 is schematic illustration of an exemplary apparatus for performing the method of FIG. 2.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0022] Exemplary embodiments of a method 200 of improving a sodium-ion battery 110 and an improved sodium-ion battery 110 will be described below with reference to FIGS. 1 to 5. In the present application, the term “sodium-ion battery” includes graphene sodium-ion batteries and other variations of sodium-ion batteries.

[0023] As shown in FIG. 1, an exemplary sodium-ion battery 110 comprises two electrodes 70 separated by a volume (or “sea”) of an electrolyte 30 that ionically connects the two electrodes 70 with positive sodium ions 50. To avoid shorting, an ion-permeable separator 40 may be provided in the volume of the electrolyte 30 between the cathode 10 and the anode 20 to prevent contact of the cathode 10 with the anode 20. Each electrode 70 comprises a current/electron collector 90. Each current collector 90 is connected to a terminal 18, 28 of the sodium-ion battery 110. The terminals 18, 28 are provided for connection with an external circuit (not shown). The external circuit may include an external device that is to be powered by the sodium-ion battery 110, or may include an energy source to charge the sodium-ion battery 110. When the sodium-ion battery 110 has been charged and is subsequently being discharged during use to power a device, the negative electrode 70 is termed the cathode 10 and the positive electrode 70 is termed the anode 20. During fabrication of the battery 110, one of the electrodes 70 may be treated with a sodium ion compound 62 in order to serve as the cathode 10, while the other of the electrodes 70 may be treated with hard carbon 64 to serve as the anode 20.

[0024] Sodium ions 50 in the electrolyte 30 move between the two electrodes 70 during charging and discharging of the battery 110. Direction of movement of the sodium ions 50 during discharging of the battery 10 is from the negative cathode 10 to the positive anode 20 as indicated by the arrow in FIG. 1. The direction of movement of the sodium ions 50 is reversed during charging of the battery 110, i.e., from the anode 20 to the cathode 10.

[0025] As shown in FIG. 2, in the method (200) to improve the energy capacity of sodium-ion batteries, in a first step, a sodium-ion battery 110 that has a state of charge in a range of 0% to 25% is provided (210). Notably, all sodium-ion batteries initially carry no charge, i.e. a state of charge of 0%, during production and need to be charged before use. Thus, the method 200 may be performed with newly produced sodium-ion batteries before they are first charged for use. Alternatively, if a sodium-ion battery has already been charged, it may be drained to zero charge or a low level of charge so as to provide a sodium-ion battery 110 that carries a state of charge in the range of, for example, 0-25% (210) before subsequent steps of the method (200) are performed. For a sodium-ion battery 110 that has an open circuit voltage of 2.2V when fully charged, the battery may have an open circuit voltage of 0-0.55V corresponding to the state of charge range of 0-25%. The method may be applied to sodium-ion batteries having a state of charge of other ranges, such as but not limited to, 0-20%, 0-15%, 0-10%, 0-5%, 0-2.5%, 0-1.25%, etc. The method may also be applied to sodium-ion batteries having no charge, i.e. a state of charge of 0%.

[0026] After the first step of providing a sodium-ion battery that has a state of charge in the range of 0-25% (210), a first voltage is then momentarily applied to a first electrode 70 of the sodium-ion battery 110 (220). When the first voltage is momentarily applied, the first electrode 70 experiences an electric shock/pulse current that moves in one direction from the first electrode 70 to the second electrode 70. This likely results in the sodium ions 50 in the electrolyte 30 becoming more solidly or closely attached to the surface of the first electrode 70, as shown in FIG. 3B. This would increase contact surface between the sodium ions 50 and the first electrode 70, thereby allowing easier transfer of electrons between the first electrode 70 and the sodium ions 50.

[0027] Notably, after the first voltage has been applied to the first electrode 70 (220), the sodium-ion battery 110 remains uncharged or has a low state of charge of no more than a low percentage, for example, no more than 25%, because of the extremely short duration of application of the first voltage to the first electrode 70. For example, the duration of the momentary application of the first voltage may range from 1/1000 seconds to 1/2 seconds. In

an exemplary embodiment, the duration of momentary application of the first voltage may be 1/300 seconds.

[0028] In a next step, a second voltage is momentarily applied to the second electrode 70 of the sodium-ion battery 110 (240). As the sodium-ion battery 110 is still uncharged or has a relatively low state of charge after application of the first voltage to the first electrode 70 (220), there is no need to drain the sodium-ion battery 110 before applying the second voltage. When the second voltage is applied to the second electrode 70 (240), the second electrode 70 experiences an electric shock/pulse current that moves in one direction from the second electrode 70 to the first electrode 70. This again likely results in the sodium ions 50 in the electrolyte 30 becoming more solidly or closely attached to the surface of the second electrode 70. This would similarly increase a contact surface between the sodium ions 50 and the second electrode 70, thereby allowing easier transfer of electrons between the second electrode 70 and the sodium ions 50.

[0029] Similarly, the duration of the momentary application of the second voltage may range from 1/1000 seconds to 1/2 seconds. In an exemplary embodiment, the duration of momentary application of the second voltage may be 1/300 seconds. As a result of the short duration of application of the second voltage to the second electrode 70, the sodium-ion battery 110 again remains uncharged or has a low state of charge of no more than a low percentage, for example, no more than 25%, even after the second voltage has been applied to the second electrode 70 (240).

[0030] As mentioned above, every sodium-ion battery 110 initially carries no charge when it is first produced. Therefore, it has no electrical poles and does not have electrically positive or negative electrodes 70. However, when charged for use to power a device (not shown), the sodium-ion battery 110 has a cathode 10 (negative electrode) and an anode 20 (positive electrode). During production of the sodium-ion battery 110, the cathode 10 and anode 20 are each made from appropriate materials so that even when the battery 110 is not yet charged, physically and chemically it can already be discerned which electrode 70 will be the cathode 10 and which electrode 70 will be the anode 20 during use of the battery 110.

Typically, the cathode 10 in a sodium-ion battery 110 has a significantly larger surface area than the anode 20.

[0031] In the method 200, preferably, the first electrode 70 to which the first voltage is momentarily applied is the cathode 10 when the sodium-ion battery 110 is charged for use. Accordingly, the second electrode 70 to which the second voltage will be momentarily applied is the anode 20. Application of the first voltage to the cathode 10 appears to be more effective than application of the first voltage to the anode 20 because of the significantly larger surface area of the cathode 10 when compared to the anode 20. As a result of the electric shock/pulse current moving from the cathode 10 to the anode 20 during application of the first voltage, it is envisaged that positive sodium ions 50 are attracted towards the larger surfaced cathode 10 to become firmly attached to the surface of the cathode 10, thus improving electron transfer between the electrolyte 30 and the cathode 10. At the same time, it is envisaged that the surface of the anode 20 (which is often made of hard carbon) is being cleaned as microscopic dirt surface is carried by the sodium ions 50 from the surface of the anode 20 into the sea of electrolyte 30, thereby reducing negative impact of microscopic dirt on the anode 20.

[0032] In the method 200, as mentioned above, the electric shock/pulse current that is experienced by the first and second electrodes 70 during application of the first and second voltages respectively moves in only one direction, like a direct current (DC) as shown in FIGS. 4A and 4B. Thus, if an alternating current (AC) power source having a sine wave form as shown in FIG. 4C is used to apply the first and/or second voltages, the AC must first be rectified to a half-wave rectified AC voltage having a half sine wave form as shown in FIGS. 4D and 4E before it is applied to the electrode 70. Alternatively, the AC voltage may be rectified to a half rectangular wave form as shown in FIGS. 4G and 4F. If a DC power source is used to apply the first and/or second voltages, the DC voltage is preferably modified to have a half rectangular wave form as shown in FIGS. 4F and 4G. The rectified AC and modified DC can be combined for applying the electric shock/pulse current to the first and second electrodes 70 as long as the pole in question is on the same side, as shown in FIGS. 4H and 4I.

[0033] It should be noted that this application discloses an empirical discovery of a method for improving a sodium-ion battery such that its energy capacity is significantly improved. The above description provide only one possible explanation via Figs 3A and 3B of how the energy capacity is likely improved. Other aspects of the sodium-ion battery may also be improved. These include, but is not limited to, the initial coulombic efficiency, which could be low in existing sodium-ion batteries owing to defects on the hard-carbon anode and presence of nanopores on the anode surface. The observed results of this new method indicate that the method might also be able to overcome the defects and nanopores of the anode leading to an improved initial coulombic efficiency.

[0034] To perform the method 200, an exemplary apparatus 300 for applying the first and second voltages to the electrodes 70 of the sodium-ion battery 110 may comprise an AC/DC switchable power supply 310 connected to a DC Converter and/or AC Inverter 320 as shown in FIG. 5. The DC converter and/or AC Inverter 320 should be capable of adjusting the charge time, the voltage applied, the current during voltage application, and the form or shape of the voltage wave form that is applied to the electrode 70. During application of the first voltage to the first electrode 70 (which for example is the cathode 10), the DC converter and/or AC Inverter 320 is connected to both electrodes 70 such that the electric shock/pulse current moves in one direction from the first electrode 70 (cathode 10) to the second electrode 70 (anode 20). Similarly, during application of the second voltage to the second electrode 70 (which in the same example is the anode 20), the DC converter and/or AC Inverter 320 is connected to both electrodes 70 such that the electric shock/pulse current moves in one direction from the second electrode 70 (anode 20) to the first electrode 70 (cathode 10).

[0035] If desired to obtain better results, the step of momentarily applying the first voltage to the first electrode 70 (220) may be repeated after the second voltage has been applied to the second electrode 70. The step of momentarily applying the second voltage to the second electrode 20 (240) may also be repeated after the first voltage has been applied for the second time to the first electrode 70 to further improve results. If any electrical charge is observed by measuring the sodium ion battery's own voltage after the second voltage has been applied, the sodium ion battery should be drained of charge before repeating the step of momentarily applying the first voltage to the first electrode 70 (220) as mentioned above.

[0036] In a test that was conducted, a sodium-ion battery 110 having a factory specification charge storage capacity of 2,300 mAh was treated using the method 200 described above, wherein the first voltage of 70V was applied to the cathode 10 while the battery 110 was yet uncharged, and the second voltage of 70V was applied to the anode 20 after application of the first voltage. Both the first and second voltages applied were rectangular DC as shown in FIG. 4A. The current during application of the first and second voltages was estimated to be 3A.

[0037] Before treatment using the method 200, after discharging the fully charged battery 110 to 2V at the rate of 1C, it was observed that the battery capacity was 2020 mAh. After treatment, the improved sodium-ion battery was found to be able to store a charge of 2320 mAh, which is an improvement of 14.8%.

[0038] Notably, in the test that was conducted, although the exemplary first and second voltages applied were 70V and 70V respectively and the duration of their application was 1/300 seconds, it will be appreciated that other voltages and other durations of voltage application that have been determined to further improve performance of the sodium-ion battery may be used in the disclosed method 200. For example, the first and second voltages may range from 0.5V to 300V. Current (amperes) during application of the first and second voltages may range from 0.1A to 1,000A.

[0039] While there has been described in the foregoing description exemplary embodiments of the present invention, it will be understood by those skilled in the technology concerned that many variations in details of design, construction and/or operation may be made without departing from the present invention.

CLAIMS

1. A method of improving a sodium-ion battery, the method comprising:
 - a) momentarily applying a first voltage to a first electrode of a sodium-ion battery having a state of charge in a range of 0-25%; and
 - b) momentarily applying a second voltage to a second electrode of the sodium-ion battery.
2. The method of claim 1, wherein the first voltage and the second voltage each has one of: a DC rectangular wave form, a half sine wave form, and a combination of a DC rectangular wave form and a half sine wave form.
3. The method of claim 1 or claim 2, further comprising, after step b), repeating step a).
4. The method of claim 3, further comprising, after repeating step a), repeating step b).
5. The method of any one of claims 1 to 4, wherein the first electrode is a negative electrode of the sodium-ion battery when the sodium-ion battery is charged for use and wherein the second electrode is a positive electrode of the sodium-ion battery when the sodium-ion battery is charged for use.
6. The method of any one of claims 1 to 5, wherein the sodium-ion battery has a state of charge of 0% and momentarily applying the first voltage in step a) is configured such that the sodium-ion battery remains uncharged after the first voltage has been momentarily applied.
7. The method of any one of claims 1 to 6, wherein the sodium-ion battery has a state of charge of 0% and momentarily applying the second voltage in step b) is configured such that the sodium-ion battery remains uncharged after the second voltage has been momentarily applied.
8. The method of any one of claims 1 to 7, wherein the first voltage and the second voltage each ranges from 0.5V to 300V.

9. The method of any one of claims 1 to 8, wherein current during application of each of the first voltage and the second voltage ranges from 0.1A to 1,000A.
10. The method of any one of claims 1 to 9, wherein a duration of application of the first voltage and duration of application of the second voltage each ranges from 1/1000 seconds to 1/2 seconds.
11. The method of any one of claims 1 to 10, wherein the sodium-ion battery that has a state of charge of 0% is a newly produced sodium-ion battery before it is first charged for use.
12. An improved sodium-ion battery comprising:
 - a first electrode to which a first voltage has been momentarily applied when the sodium-ion battery has a state of charge in a range of 0-25%; and
 - a second electrode to which a second voltage has been momentarily applied when the sodium-ion battery has a state of charge in a range of 0-25%.
13. The improved sodium-ion battery of claim 12, wherein the first voltage and the second voltage each has one of: a DC rectangular wave form, a half sine wave form, and a combination of a DC rectangular wave form and a half sine wave.
14. The improved sodium-ion battery of claim 12 or claim 13, wherein the first electrode is a negative electrode of the sodium-ion battery when the sodium-ion battery is charged for use and wherein the second electrode is a positive electrode of the sodium-ion battery when the sodium-ion battery is charged for use.
15. The improved sodium-ion battery of any one of claims 12 to 14, wherein the sodium-ion battery has a state of charge of 0% and remains uncharged after the first voltage had been momentarily applied.

16. The improved sodium-ion battery of any one of claims 12 to 15, wherein the sodium-ion battery has a state of charge of 0% and remains uncharged after the second voltage has been momentarily applied.
17. The improved sodium-ion battery of any one of claims 12 to 16, wherein the first voltage and the second voltage each ranges from 0.5V to 300V.
18. The improved sodium-ion battery of any one of claims 12 to 17, wherein current during application of each of the first voltage and the second voltage ranges from 0.1A to 1,000A.
19. The improved sodium-ion battery of any one of claims 12 to 18, wherein a duration of application of the first voltage and of the second voltage ranges from 1/1000 seconds to 1/2 seconds.
20. The improved sodium-ion battery of any one of claims 12 to 19, wherein the sodium-ion battery that has a state of charge of 0% is a newly produced sodium-ion battery before it was first charged for use.

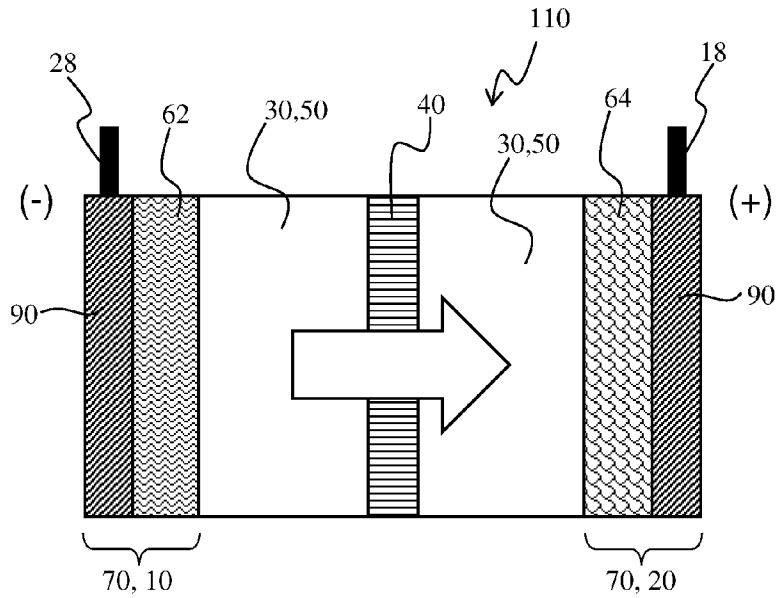


FIG. 1

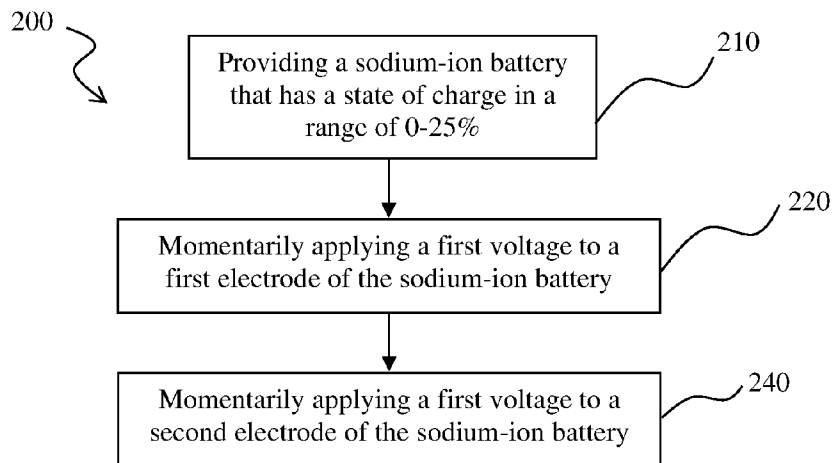


FIG. 2

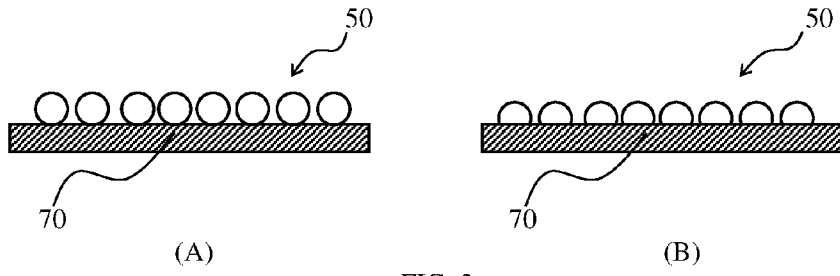


FIG. 3

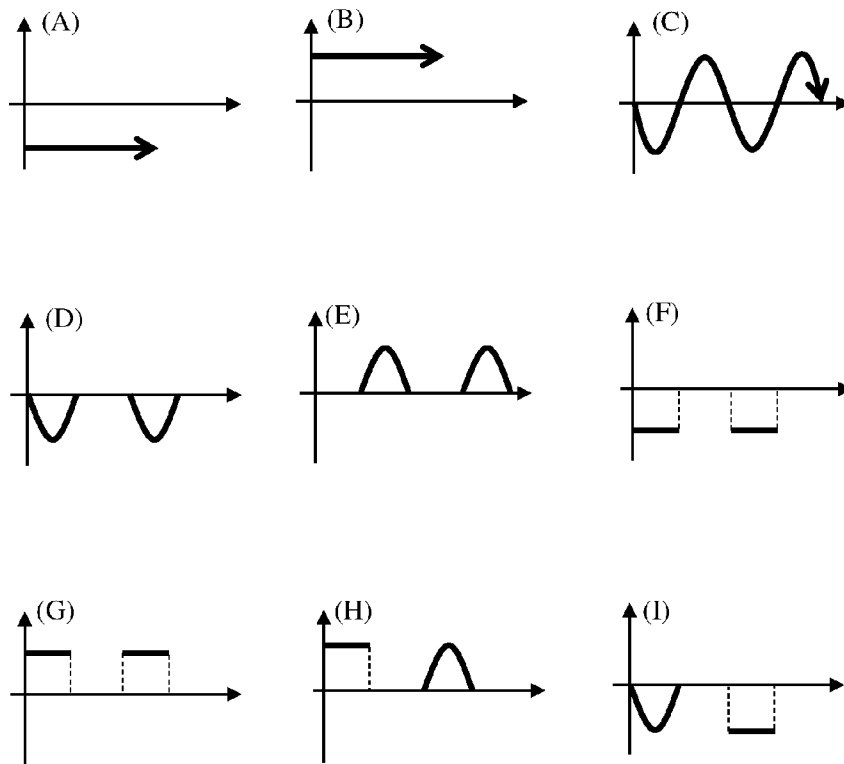


FIG. 4

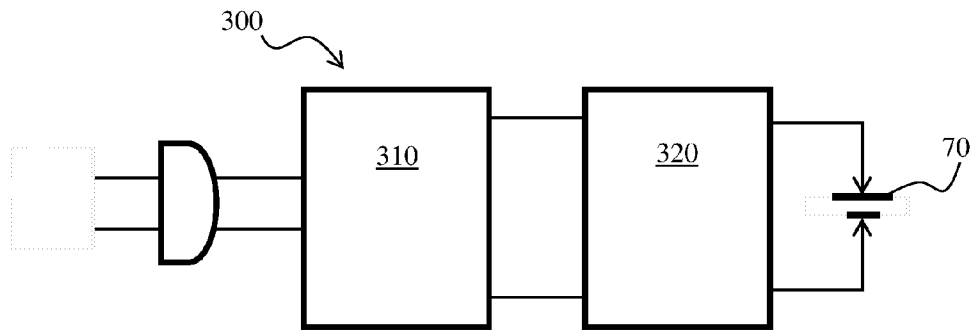



FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.

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A. CLASSIFICATION OF SUBJECT MATTER		
See Supplemental Box		
According to International Patent Classification (IPC)		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
H01M		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
FAMPAT, COMPENDEX, INSPEC: sodium ion batteries, pulse, instant, momentary, transient, voltage, electrical potential difference, current, negative electrode, anode, hard carbon, positive electrode, cathode, alternating, bidirectional, forward, reverse, charging, discharging, volt, C-rate, seconds, frequency, Hz, solid electrolyte interface film, SEI film, passivation film, stability, defects, energy capacity, capacity loss, cycle life, polarization, 钠离子电池, 脉冲, 瞬时, 电压, 电位差, 电流, 负极, 阳极, 硬碳, 正极, 阴极, 交替, 双向, 正向, 反向, 充电, 放电, 伏特, C 倍率, 秒, 频率, 赫兹, 固体电解质界面膜, 钝化膜, 稳定性, 缺陷, 能量容量, 容量损失, 循环寿命, 极化 and similar terms.		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 1251953 A (ZHONG YANG) 3 May 2000 see the whole document, in particular paragraph [0004]-[0008], [0012]-[0017], [0026], [0040]-[0065], [0084]-[0086] and [0111] and Fig. 1-4 and 8-9 of the machine translation	1-20
A	CN 114976267 A (NANJING VOCATIONAL UNIV OF INDUSTRY TECHNOLOGY) 30 August 2022 see the whole document, in particular paragraph [0002]-[0006] and claim 1 of the machine translation	1-20
P,X	CN 117080593 A (HUZHOU CHAONA NEW ENERGY TECH CO LTD) 17 November 2023 see the whole document, in particular paragraph [0002]-[0006] and [0030]-[0045] and Fig. 1-2 and 6 of the machine translation	1-20
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		

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Date of the actual completion of the international search 25/06/2024 (day/month/year)	Date of mailing of the international search report 04/07/2024 (day/month/year)	
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	CN 117039216 A (LISHEN QINGDAO NEW ENERGY CO LTD) 11 October 2023 see the whole document, in particular paragraph [0002]-[0004] and example 1 of the machine translation	1-20
P,X	CN 117638272 A (JIAN UTILITY TECH CO LTD) 1 March 2024 see the whole document, in particular paragraph [0003]-[0005] and example 1 of the machine translation	1-20
P,A	CN 116365004 A (SHENZHEN YUJIAOCHENG TECH CO LTD) 30 June 2023 see the whole document, in particular paragraph [0003]-[0005] and claim 1 of the machine translation	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/SG2024/050163

Note: This Annex lists known patent family members relating to the patent documents cited in this International Search Report. This Authority is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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CN 117080593 A	17/11/2023	NONE	
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