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61/903,739 13 November 2013 (13.11.2013) US(71) Applicant: **MASSACHUSETTS INSTITUTE OF TECHNOLOGY** [US/US]; 77 Massachusetts Avenue, Cambridge, MA 02139 (US).

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[Continued on next page]

(54) Title: METAL SULFIDE ELECTRODES AND ENERGY STORAGE DEVICES THEREOF

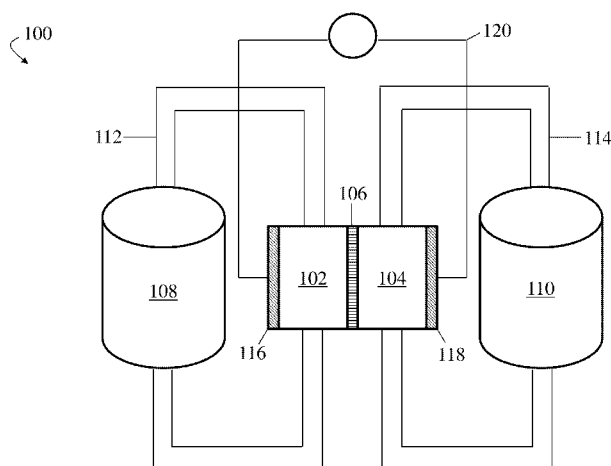


FIG. 1A

(57) Abstract: The present invention generally relates to energy storage devices, and to metal sulfide energy storage devices in particular. Some aspects of the invention relate to energy storage devices comprising at least one flowable electrode, wherein the flowable electrode comprises an electroactive metal sulfide material suspended and/or dissolved in a carrier fluid. In some embodiments, the flowable electrode further comprises a plurality of electronically conductive particles suspended and/or dissolved in the carrier fluid, wherein the electronically conductive particles form a percolating conductive network. An energy storage device comprising a flowable electrode comprising a metal sulfide electroactive material and a percolating conductive network may advantageously exhibit, upon reversible cycling, higher energy densities and specific capacities than conventional energy storage devices.



— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

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6 November 2014

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2014/014681

A. CLASSIFICATION OF SUBJECT MATTER

INV. H01M8/18 H01M8/22
ADD.

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

B. FIELDS SEARCHED

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

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 376 123 B1 (CHU MAY-YING [US]) 23 April 2002 (2002-04-23) paragraph [0126] paragraph [0075] - paragraph [0076] paragraph [0085] - paragraph [0088] paragraph [0090] - paragraph [0091] paragraph [0092] - paragraph [0093] paragraph [0097] paragraph [0098] paragraph [0100] paragraph [0122] paragraph [0139] paragraph [0143] paragraph [0146] paragraph [0152] example 3 paragraph [0145] paragraph [0148] paragraph [0130] -/--	1-55,87, 89,90



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

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

"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

International application No

PCT/US2014/014681

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	claims 1, 12, 24, 44 paragraph [0183] - paragraph [0184] paragraph [0243] - paragraph [0247] paragraph [0096] paragraph [0014] ----- VICTOR E BRUNINI ET AL: "Modeling the hydrodynamic and electrochemical efficiency of semi-solid flow batteries", ELECTROCHIMICA ACTA, ELSEVIER SCIENCE PUBLISHERS, BARKING, GB, vol. 69, 2 March 2012 (2012-03-02), pages 301-307, XP028407102, ISSN: 0013-4686, DOI: 10.1016/J.ELECTACTA.2012.03.006 [retrieved on 2012-03-10] page 301, column 1, line 1 - page 302, column 1, line 11 page 302, column 2, line 6 - line 46 figures 1,3 table 1	1-55, 87-90
	----- US 2012/135278 A1 (YOSHIE TOMOHISA [JP] ET AL) 31 May 2012 (2012-05-31) figure 1 paragraph [0001] paragraph [0009] paragraph [0003] - paragraph [0004] paragraph [0031] - paragraph [0033] paragraph [0044] paragraph [0084] - paragraph [0086] paragraph [0088] paragraph [0090] paragraph [0093] - paragraph [0095] paragraph [0121] paragraph [0124] - paragraph [0126] paragraph [0129] - paragraph [0130]	87-90
X,P	----- FRANK Y. FAN ET AL: "Polysulfide Flow Batteries Enabled by Percolating Nanoscale Conductor Networks", NANO LETTERS, vol. 14, no. 4, 9 April 2014 (2014-04-09), pages 2210-2218, XP055120132, ISSN: 1530-6984, DOI: 10.1021/nl500740t the whole document ----- -/--	1-55, 87-90

INTERNATIONAL SEARCH REPORT

International application No

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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.
A	SHU-RU CHEN ET AL: "Ordered mesoporous carbon/sulfur nanocomposite of high performances as cathode for lithiumsulfur battery", ELECTROCHIMICA ACTA, ELSEVIER SCIENCE PUBLISHERS, BARKING, GB, vol. 56, no. 26, 2 March 2011 (2011-03-02), pages 9549-9555, XP028320982, ISSN: 0013-4686, DOI: 10.1016/J.ELECTACTA.2011.03.005 [retrieved on 2011-03-08] page 9549, column 1, line 12 - column 2, line 4 page 9550, column 1, paragraph 2 - column 2, paragraph 4 page 9553, column 1, line 13 - column 2, line 14 -----	1-55, 87-90

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/014681

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-55, 87-90

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-55, 87-90

An energy storage device, comprising: a first flowable electrode (catholyte) comprising an electrode composition comprising: a first electroactive material comprising sulfur or a metal sulfide, wherein the first electroactive material is suspended and/or dissolved in a fluid; and electronically conductive carbon (nano) particles suspended in the fluid, the electronically conductive particles forming a percolating conductive network; and a second electrode in electrochemical communication with the first electrode and a method of operating this energy storage device

2. claims: 56-86

An energy storage device, comprising: a first electrode comprising an electrode composition comprising a first electroactive material comprising sulfur, wherein the first electroactive material is suspended and/or dissolved in a fluid, wherein the concentration of sulfur is at least about 2 M; and a second electrode in electrochemical communication with the first electrode, wherein the second electrode comprises a second electroactive material comprising an electroactive metal or metal alloy comprising a non-sulfur element, wherein both electrodes of the energy storage device are substantially fluid prior to first use, characterised by further comprising a layer adjacent the second electrode of the energy storage device, wherein the layer comprises LiNO_3 , a ceramic and or a polymer.

3. claims: 91-95

A method of operating an energy storage device, comprising the steps of:
reversibly cycling an energy storage device containing a flowable electrode such that a metal sulfide is precipitated and subsequently dissolved in the flowable electrode during the cycling wherein the precipitated and dissolved metal sulfide comprises Li_2S , wherein the reversible cycling occurs over a voltage range of from about 0.45 V to about 2.7 V, wherein the flowable electrode of the energy storage device is in motion during at least a portion of the cycling and wherein reversible cycling of the energy storage device comprises: transporting the flowable electrode through an electrode compartment; inhibiting the flow of the flowable electrode; at least partially charging or discharging a portion of the flowable electrode; and transporting the flowable electrode out of the electrode compartment.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2014/014681

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6376123	B1	23-04-2002	NONE

US 2012135278	A1	31-05-2012	CN 102804470 A 28-11-2012
			JP 5417441 B2 12-02-2014
			US 2012135278 A1 31-05-2012
			WO 2010143634 A1 16-12-2010
