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(54) Title: LITHIUM-SULPHUR CELL

(57) Abstract: The present invention relates to a lithium-sulphur cell comprising an anode comprising lithium metal or lithium metal alloy;a cathode comprising a mixture of electroactive sulphur material and solid electroconductive material; and a liquid electrolyte comprising at least one lithium salt and a solvent comprising a dinitrile.

LITHIUM-SULPHUR CELL

[0001] The present invention relates to a lithium-sulphur cell.

BACKGROUND

[0002] A typical lithium-sulphur cell comprises an anode (negative electrode) formed from lithium metal or a lithium metal alloy, and a cathode (positive electrode) formed from elemental sulphur or other electroactive sulphur material. The sulphur or other electroactive sulphur-containing material may be mixed with an electrically conductive material, such as carbon, to improve its electrical conductivity. Typically, the carbon and sulphur are ground and then mixed with a solvent and binder to form a slurry. The slurry is applied to a current collector and then dried to remove the solvent. The resulting structure is calendared to form a composite structure, which is cut into the desired shape to form a cathode. A separator is placed on the cathode and a lithium anode placed on the separator. Electrolyte is introduced into the cell to wet the cathode and separator. The electrolyte typically includes an electrolyte salt dissolved in a solvent.

[0003] Lithium-sulphur cells are secondary cells, and may be recharged by applying an external current to the cell. Rechargeable cells of this type have a wide range of potential applications. Important considerations when developing lithium-sulphur secondary cells include gravimetric energy, cycle life and ease of cell assembly.

[0004] When a lithium-sulphur cell is discharged, the sulphur in the cathode is reduced in two-stages. In the first stage, the electroactive sulphur material (e.g. elemental sulphur) is reduced to polysulphide species, S_n^{2-} ($n \geq 2$). These species are generally soluble in the electrolyte. In the second stage of discharge, the polysulphide species are reduced to lithium sulphide, Li_2S, which is insoluble. When the cell is charged, the two-stage mechanism occurs in reverse, with the lithium sulphide being oxidised to lithium polysulphide and thereafter to lithium and sulphur.

As well as being a suitable solvent for the electrolyte salt, a solvent for use in lithium sulphur cell should not react with the lithium metal anode and act as a good solvent for the polysulphide species formed upon discharge. As such, the solvent requirements of lithium-sulphur cells are significantly more complex than those of a lithium-ion cell because of the multi-dimensionality introduced at least in part by the intermediate species formed during the charge and discharge of a lithium sulphur cell. Many solvents, such as carbonates, that are typically employed in lithium-ion cells are unsuitable for use in lithium-sulphur cells because they react with the polysulphides formed upon discharge, particularly at high sulphur

loadings. The performance of an electrolyte solvent in a lithium-sulphur cell, therefore, cannot be predicted from its performance as an electrolyte solvent in a lithium-ion cell.

Description

[0005] Before particular examples of the present invention are described, it is to be understood that the present disclosure is not limited to the particular cell, method or material disclosed herein. It is also to be understood that the terminology used herein is used for describing particular examples only and is not intended to be limiting, as the scope of protection will be defined by the claims and equivalents thereof.

[0006] In describing and claiming the cell and method of the present invention, the following terminology will be used: the singular forms "a", "an", and "the" include plural forms unless the context clearly dictates otherwise. Thus, for example, reference to "an anode" includes reference to one or more of such elements.

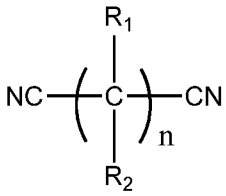
[0007] According to one aspect of the present invention, there is provided a lithium-sulphur cell comprising:

an anode comprising lithium metal or lithium metal alloy;
a cathode comprising a mixture of electroactive sulphur material and solid electroconductive material; and
a liquid electrolyte comprising at least one lithium salt and a solvent comprising a dinitrile.

[0008] In embodiments of the present invention, it has been found that, by using a dinitrile as an electrolyte solvent, the gravimetric energy of the lithium sulphur cell can be increased. It has also been found that electrolytes formed using dinitriles as solvent may also have favourable viscosity characteristics. Accordingly, such electrolytes can be applied to the cathode in a convenient and efficient manner, facilitating efficient and convenient cell assembly. In embodiments of the present invention, it has also been found that the cycle life of a lithium sulphur cell may also be improved by using a dinitrile as a solvent in the lithium sulphur cell.

[0009] In embodiments of the present invention, it has also been found that the low temperature performance of the lithium sulphur cell may be improved using a dinitrile as a solvent. For example, in certain embodiments, the electrolyte may remain in liquid form at temperatures below 0 degrees C, for instance, below -10 degrees C (e.g. up to -30 degrees C).

[0010] The dinitrile may have the formula (I):



(I)

wherein:

n is an integer 2 to 10, and

in each $-CR_1R_2-$ linkage, R_1 and R_2 are each independently selected from H, -OH, amine, amide, ether and a C_1 to C_6 alkyl group.

[0011] For the avoidance of doubt, each $-CR_1R_2-$ linkage may be the same or different. In one embodiment, one of the $-CR_1R_2-$ linkages is different from the remainder of the $-CR_1R_2-$ linkages in the dinitrile. The $-CR_1R_2-$ linkage that is different from the remaining $-CR_1R_2-$ linkages may be present adjacent a CN group.

[0012] Where R_1 and/or R_2 is an amine, the amine may have the formula $-NR_aR_b$, where each of R_a and R_b is independently H or a hydrocarbyl group. Suitable hydrocarbyl groups include alkyl groups, for example, C_1 to C_4 alkyl (e.g. methyl, ethyl, propyl or butyl). For example, $-NR_aR_b$ may be $-NH_2$ or $-N(CH_3)_2$. The amine may be a primary, secondary or tertiary amine group.

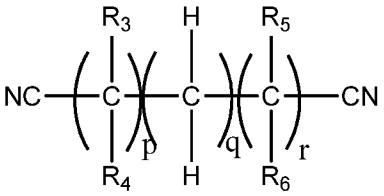
[0013] Where R_1 and/or R_2 is an amide, the amide may be $-NR_aC(O)R_b$, where each of R_a and R_b is independently H or a hydrocarbyl group. Suitable hydrocarbyl groups include alkyl groups, for example, C_1 to C_4 alkyl (e.g. methyl, ethyl, propyl or butyl). For example, $-NR_aC(O)R_b$ may be $-NHC(O)CH_3$.

[0014] Where R_1 and/or R_2 is an ether group, the ether may have the formula $-OR_c$, where R_c is a hydrocarbyl group. Suitable hydrocarbyl groups include alkyl groups, for example, C_1 to C_4 alkyl (e.g. methyl, ethyl, propyl or butyl). For example, the $-OR_c$ group may be $-OCH_3$.

[0015] Where R_1 and/or R_2 is an alkyl group, the alkyl group may be a C_1 to C_6 alkyl group, for example, methyl, ethyl, propyl, i-propyl, n-butyl, i-butyl and t-butyl, pentyl or hexyl.

[0016] In one embodiment, the dinitrile of formula (I) includes at least 2, for example, 2 to 4 $-CR_1R_2-$ linkages that are of the formula $-CH_2-$. Optionally, the dinitrile of formula (I) may also include one or two $-CR_1R_2-$ linkages of the formula $-CHR_2$. The $-CHR_2-$ linkage may be adjacent a –CN group.

[0017] In one embodiment, the dinitrile has the formula (II):



(II)

wherein:

p is 0 or 1,

q is an integer of 1 to 9,

r is 0 or 1, and

[0018] R_3, R_4, R_5 and R_6 are each independently selected from H and a C_1 to C_6 alkyl group (e.g. methyl, ethyl, propyl, i-propyl, n-butyl, i-butyl and t-butyl, pentyl or hexyl, preferably, methyl).

[0019] Preferably, at least one of R_3 and R_4 is H, and at least one of R_5 and R_6 is H. Preferably, at least one of R_3, R_4, R_5 and R_6 is a C_1 to C_6 alkyl group. In one embodiment, R_3 is H; R_5 is H; and at least one of R_4 and R_6 is a C_1 to C_6 alkyl group. For example, in one embodiment, R_3 is H; R_5 is H; R_4 is H and R_6 is a C_1 to C_6 alkyl group.

[0020] In one embodiment, p is 0 and r is 1. In one embodiment, q is 2. For example, p may be 0, r may be 1 and q may be 2.

[0021] Examples of suitable dinitriles include 2-methylglutaronitrile, succinonitrile and adiponitrile.

[0022] As described above, the electrolyte also comprises a lithium salt. Suitable lithium salts include at least one of lithium hexafluorophosphate ($LiPF_6$), lithium hexafluoroarsenate ($LiAsF_6$), lithium perchlorate ($LiClO_4$), lithium trifluoromethanesulfonimide ($LiN(CF_3SO_2)_2$)), lithium borofluoride ($LiBF_4$), lithium trifluoromethanesulphonate (CF_3SO_3Li), and lithium bis(oxalato)borate ($LiB(C_2O_4)_2$). Preferably the lithium salt is lithium trifluoromethanesulfonimide ($LiN(CF_3SO_2)_2$)).

[0023] The concentration of lithium salt in the electrolyte is preferably 0.1 to 5M, more preferably 0.2 to 3M, for example, 0.4 to 2 M (e.g. 0.5 to 1M).

[0024] As discussed above, the lithium sulphur cell of the present invention includes an anode, a cathode, an electrolyte and, optionally, a porous separator. The latter may be positioned between the anode and the cathode. The anode is formed of lithium metal or a lithium metal alloy. Preferably, the anode is a metal foil electrode, such as a lithium foil electrode. The lithium foil is formed of lithium metal or lithium metal alloy.

[0025] The cathode of the cell includes a mixture of electroactive sulphur material and electroconductive material. This mixture forms an electroactive layer, which may be placed in contact with a current collector.

[0026] The electroactive sulphur material may comprise elemental sulphur, sulphur-based organic compounds, sulphur-based inorganic compounds and sulphur-containing polymers. Preferably, elemental sulphur is used.

[0027] The solid electroconductive material may be any suitable conductive material. Preferably, this solid electroconductive material may be formed of carbon. Examples include carbon black, carbon fibre, graphene and carbon nanotubes. Other suitable materials include metal (e.g. flakes, filings and powders) and conductive polymers. Preferably, carbon black is employed.

[0028] The mixture of electroactive sulphur material and electroconductive material may be applied to the current collector in the form of a slurry in a solvent (e.g. water or an organic solvent). The solvent may then be removed and the resulting structure calendared to form a composite structure, which may be cut into the desired shape to form a cathode. A separator may be placed on the cathode and a lithium anode placed on the separator. Electrolyte may then be incorporated into the assembled cell to wet the cathode and separator.

[0029] Alternatively, following the formation of the cathode, the electrolyte may be coated onto the cathode. The separator may then be placed over the coated cathode, and the anode placed over the separator.

[0030] As mentioned above, electrolytes formed using dinitriles as solvent may also have favourable viscosity characteristics. Accordingly, such electrolytes can be applied to the cathode in a convenient and efficient manner, facilitating efficient and convenient cell assembly. In a preferred embodiment of the invention, electrolyte is incorporated into the cell assembly by coating the electrolyte on the cathode, placing the separator over the coated cathode and placing the anode over the separator. The coating may be carried out in any suitable way, for example by spraying, extruding, vacuum filling, pouring and/or spreading the electrolyte over the active sulphur material. After the electrolyte is incorporated into the cell assembly, the cell may be sealed e.g. in an enclosure. The enclosure may be water-tight and/or air-tight. Suitable enclosures include pouches.

[0031] Where a separator is employed, the separator may comprise any suitable porous substrate that allows ions to move between the electrodes of the cell. The separator should be positioned between the electrodes to prevent direct contact between the electrodes. The porosity of the substrate should be at least 30%, preferably at least 50%, for example, above

60%. Preferably, the porosity of the separator is 40-60%, more preferably 45-55%, for example 50%. Suitable separators include a mesh formed of a polymeric material. Suitable polymers include polypropylene, nylon and polyethylene. Non-woven polypropylene is particularly preferred. It is possible for a multi-layered separator to be employed.

[0032] Preferably, the separator is selected from non-woven polypropylene and polyethylene.

[0033] Preferably, the permeability of the separator is less than 300 Gurley, more preferably less than 250 Gurley, for example 200 Gurley.

[0034] The lithium sulphur cell of the present invention is a secondary cell. When the lithium-sulphur cell is discharged, the sulphur in the cathode is reduced in two-stages. In the first stage, the electroactive sulphur material (e.g. elemental sulphur) is reduced to polysulphide species, S_n^{2-} ($n \geq 2$). These species are generally soluble in the electrolyte. In the second stage of discharge, the polysulphide species are reduced to lithium sulphide, Li_2S, which, typically, deposits on the surface of the anode.

[0035] When the cell is charged, the two-stage mechanism occurs in reverse, with the lithium sulphide being oxidised to lithium polysulphide and thereafter to lithium and sulphur. The electrolyte of the cell, therefore, may include polysulphide species dissolved in the dinitrile.

Example 1

[0036] All electrolytes were prepared by dissolving lithium bis(trifluoromethylsulfonyl)imide salt (LiTFSI) into the solvents listed in the table below at a concentration of 0.5M. Electrolytes were then stirred at 30 °C for 1 h or until completely dissolved.

[0037] The electrolytes were then incorporated into cells assembled under dry room conditions (dew point < -50 °C). Cathode material was composed of sulfur, carbon black and polyethylene oxide binder (PEO) at a ratio of 70:10:20 (w/w), respectively. The cathode material was cast onto carbon-coated aluminium foil with a typical surface capacity of 1.9–2.0 mAh/cm^2. Cells were assembled by wetting the cathode with the electrolyte (3.5 µL/mAh/cm^2), which was stacked in turn with a polypropylene separator(Celgard 3501) and 100 µm thick lithium foil anode.

[0038] Discharge-charge performances of the cells were evaluated in galvanostatic mode using a Maccor multi-channel cycler with a voltage range of 1.5–2.45 V at 30°C. The cells were discharged and charged at current densities of 0.2C and 0.1C, respectively.

[0039] The table below shows the gravimetric energy density achieved with each cell. This was compared to a reference cell formed using 0.5M lithium bis(trifluoromethylsulfonyl)imide

salt (LiTFSI) in sulfolane. As can be seen from the table, the cells formed using dinitriles as electrolyte solvents showed significantly improved gravimetric energy densities compared to the reference cell and cells formed using mononitriles as electrolyte solvents.

[0040] Cell Composition	0.5M LiTFSI in sulfolane	0.5M LiTFSI in 2-MGN	0.5M LiTFSI in 3-MPN	0.5M LiTFSI in adiponitrile	0.5M LiTFSI in 3-(dimethyl)aminopropionitrile	0.5M LiTFSI in benzonitrile	0.5M LiTFSI in glutaronitrile
Gravimetric Energy Density, Wh/kg	173.40	192.16	177.72	199.73	151.10	95.96	190.61
% of standard (gravimetric energy density)	100.00%	110.82%	102.49%	115.18%	87.14%	55.34%	109.93%

MPN = 3-methoxypropionitrile

MGN = 2-methylglutaronitrile

Example 2

A lithium sulphur cell formed using lithium LiTDI (4,5-dicyano-2-(trifluoromethyl)imidazolium) in 2-methylglutaronitrile as an electrolyte was cycled at temperatures ranging from -10 to 30 degrees C. The charge-discharge curves at the various temperatures are shown in Figure 1. A comparative cell was formed using sulfolane as an electrolyte solvent. The comparative charge-discharge curves are shown in Figure 2. As can be seen from the figures, the cell formed using 2-MGN as an electrolyte solvent has a superior performance at low temperatures.

Claims

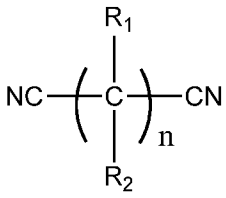
1. A lithium-sulphur cell comprising

an anode comprising lithium metal or lithium metal alloy;

a cathode comprising a mixture of electroactive sulphur material and solid electroconductive material; and

a liquid electrolyte comprising at least one lithium salt and a solvent comprising a dinitrile.

2. A cell as claimed in claim 1, wherein the dinitrile has the formula (I):



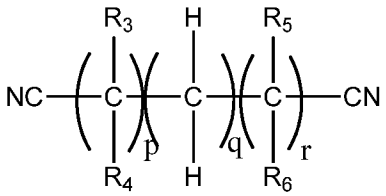
(I)

wherein:

n is an integer 2 to 10, and

in each $-CR_1R_2-$ linkage, R_1 and R_2 are each independently selected from H, -OH, amine, amide, ether and a C_1 to C_6 alkyl group.

3. A cell as claimed in claim 2, wherein the dinitrile has the formula (II):



(II)

wherein:

p is 0 or 1,

q is an integer of 1 to 9,

r is 0 or 1, and

R_3, R_4, R_5 and R_6 are each independently selected from H and a C_1 to C_6 alkyl group.

4. A cell as claimed in claim 3, wherein at least one of R_3 and R_4 is H, and at least one of R_5 and R_6 is H.
5. A cell as claimed in claim 3 or 4, wherein at least one of R_3, R_4, R_5 and R_6 is a C_1 to C_6 alkyl group.
6. A cell as claimed in any one of claims 3 to 5, wherein p is 0 and r is 1.
7. A cell as claimed in claim 6, wherein q is 2.
8. A cell as claimed in claim 6 or 7, wherein at least one of R_5 and R_6 is H and the other is a $C_1$to C_6 alkyl.
9. A cell as claimed in any one of claims 2 to 8, wherein the C_1 to C_6 alkyl group is methyl.
10. A cell as claimed in claim 1, wherein the dinitrile is selected from at least one of 2-methylglutaronitrile, succinonitrile and adiponitrile.
11. A cell as claimed in any one of the preceding claims, wherein the electrolyte further comprises lithium polysulphides dissolved in the dinitrile.
12. A cell as claimed in any one of the preceding claims, wherein the electroactive sulphur material comprises elemental sulphur.
13. A cell as claimed in any one of the preceding claims, wherein the solid electroconductive material comprises carbon.

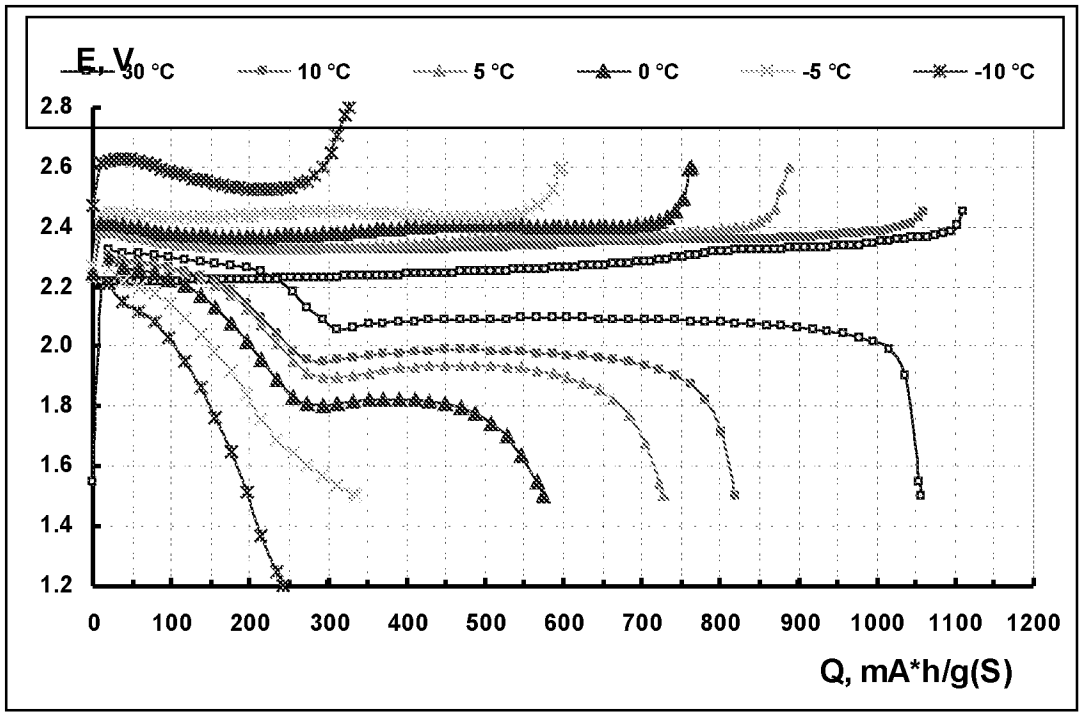


Figure 1

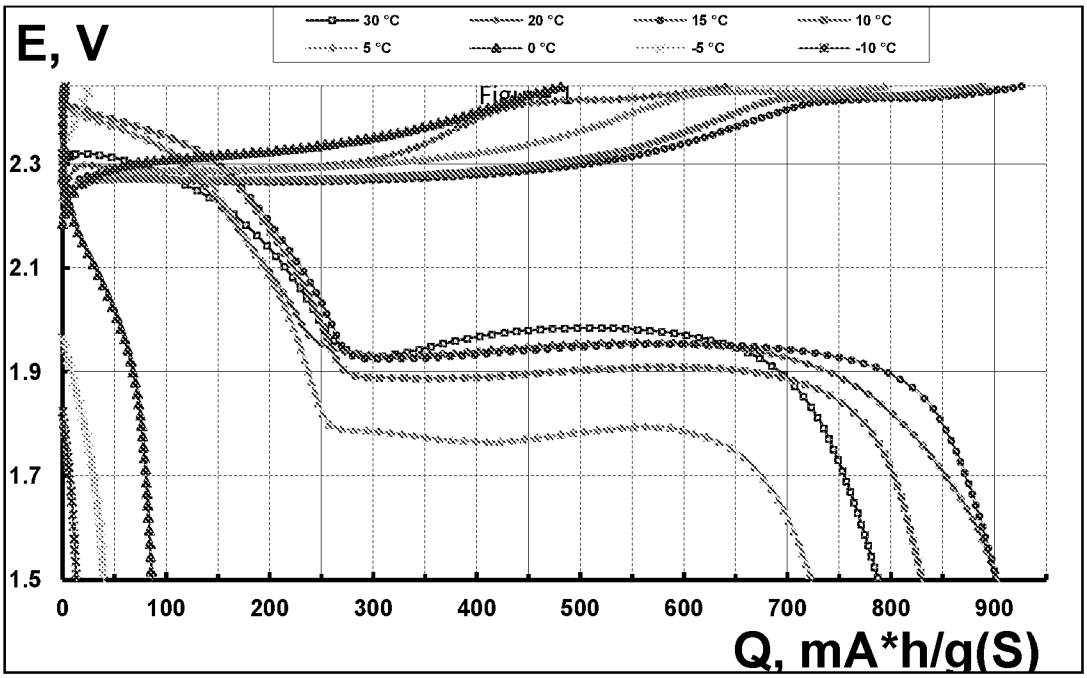


Figure 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2015/051501

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M4/38 H01M4/58 H01M10/052 H01M10/0569
ADD. H01M2/16

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	WO 2013/045561 A1 (UNIV MUENSTER WILHELMS [DE]; WINTER MARTIN [DE]; PASSERINI STEFANO [DE) 4 April 2013 (2013-04-04)	1-10,13
Y	page 15, line 16 - line 20; example 7	11,12

X	DE 10 2011 052156 A1 (UNIV JACOBS BREMEN GMBH [DE]; UNIV MUENSTER WILHELMS [DE]) 31 January 2013 (2013-01-31)	1-10
Y	paragraphs [0014], [0018]; example 4	11-13

Y	GB 2 430 542 A (OXIS ENERGY LTD [GB]) 28 March 2007 (2007-03-28) page 3, line 33 - page 4, line 10; example 1	11-13

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

☒ See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
13 August 2015	20/08/2015

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Schwake, Andree

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2015/051501

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