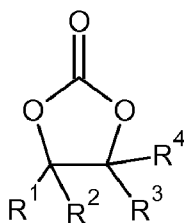


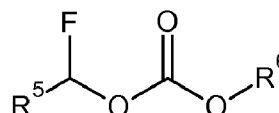


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- Published:**
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(54) **Title:** FLUORINATED CARBONATES IN HYBRID SUPERCAPACITORS



(I)



(II)

(57) **Abstract:** A hybrid supercapacitor device comprising at least one positive electrode, at least one negative electrode, a separator and an electrolyte based on one or more organic solvents wherein the electrolyte comprises from 0.1 to 100 percent by weight, based on the entire weight of the solvent(s) in the electrolyte, of at least one fluorinated carbonate of formula I or II wherein R¹ to R⁴, which may be the same or different, are independently selected from hydrogen, fluorine, C₁ to C₈-alkyl and C₁ to C₈ haloalkyl which the proviso that at least one of R¹ to R⁴ is a fluorine atom or comprises a fluorine atom and R⁵ to R⁶, independently of one another are selected from hydrogen, C₁ to C₈ alkyl or C₁-C₈ haloalkyl.

Fluorinated carbonates in hybrid supercapacitors

- [0001] This application claims priority to European application No. 12305093.2 filed on 25 Jan 2012, the whole content of this application being incorporated herein by reference for all purposes.
- [0002] The present invention relates to hybrid supercapacitors comprising fluorinated carbonates in the electrolyte system.
- [0003] A hybrid electrochemical capacitor has at least a larger capacitance electrode and a smaller capacitance electrode, with an electrolyte therebetween. The larger capacitance electrode has a larger absolute capacitance than the smaller capacitance electrode. The capacitor thus has an overall capacitance which is approximately the absolute capacitance of the smaller capacitance electrode. The electrodes are made of different materials, with the larger capacitance electrode made of material having a larger specific capacitance. The larger capacitance electrode may thus be the same physical size as or smaller than the smaller capacitance electrode.
- [0004] A hybrid supercapacitor is an electrochemical energy storage device that employs two different electrode types, the difference between the electrodes generally being in capacity or composition. Most commonly, one electrode is a redox (faradaic) electrode and the other a double-layer (non-faradaic) electrode.
- [0005] Capacitors are widely used devices for storing electrical energy. Among the various types of capacitors are electrochemical capacitors and electrolytic capacitors.
- [0006] Classical electrolytic capacitors consist of a series of combinations of two capacitors, separated by an electrolyte, and between which dielectric oxide film is formed adjacent to the surface of one or both of the electrodes.
- [0007] An electrochemical capacitor is formed by electrochemical processes (double-layer charge storage or pseudo-faradaic charge storage) across an interface, such as the interface between an electrolyte and an electrode. Such capacitors rely on charge accumulation at an interface in

order to store energy. Such capacitors do not rely on a dielectric oxide film for charge storage.

- [0008] Compared to batteries as electrical energy storage system, capacitors have a lower energy density but a higher power density, i.e. the amount of energy per mass unit which can be stored is lower than with e.g. secondary batteries, but capacitors can be discharged and recharged very quickly thus providing a high power density which is required an advantageous for certain applications. Combinations of batteries and super capacitors provide a great discharge power which is useful in conjunction with devices for the starting of various engines.
- [0009] The concept of hybrid super capacitors where one electrode is made from a rechargeable battery-type material and the other by activated carbon has been first introduced in aqueous electrolytes. Later, lithium intercalation compounds have been proposed for electrodes in symmetric capacitors using organic electrolytes.
- [0010] Aida et al., *Electrochem. & Solid state letters* 2006, 9, 534 and 2007, 10 A93, described an asymmetric capacitor with activated carbon and non-graphitizable carbon as positive and negative electrode, using LiPF₆ in ethylene carbonate/diethyl carbonate mixtures as electrolyte. The system has a poor cycle life due to the capacity loss of the non-graphitizable carbon negative electrode. This capacity loss is described to the fact that the high potential of the active carbon electrode provokes the electrolyte decomposition and formation of hydrogen fluoride. Hydrogen fluoride further reacts with the solid electrolyte interface at the negative electrode, forming lithium fluoride which blocks the electrode. To improve the performance of the system, a lithium foil was placed between the two electrodes. Although this improved the cycle life to a certain extent, there was still a significant loss in capacitance.
- [0011] It might be generally said that the use of metallic lithium provokes a number of drawbacks, in particular also from the point of view of security.
- [0012] Béguin et al. *J. Power Sources* 2008, 177, 643 proposed that the intercalated lithium can be directly taken from the electrolyte. The system described uses graphite in the negative electrode composition and

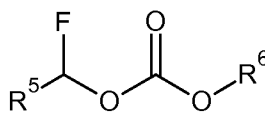
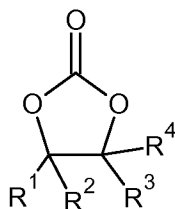
commercial activated carbon in the positive one and as electrolyte 1 mol/L of LiPF₆ in a mixture of ethylene carbonate and diethyl carbonate (1:1 wt/wt). After a special formation process of the graphite electrodes consisting in a few charge/discharge cycles, the lithium intercalation level in the electrode is such that the potential of the latter is stable at around 0.1V vs Li/Li⁺. Accordingly the systems described by Béguin et al. provide a number of advantages: metallic lithium is not used, the potential of the negative electrode is kept stable during working of the cell and no Li plating takes place and a good cycle life is obtained in addition to the high energy density and high power density of the cell. The energy density of the system is higher than that of an electrochemical double layer capacitor, however, due to the non-optimized nature of the electrolyte and electrode materials, improvement of electrical performances by developing the components to design them perfectly for the desired should still be possible.

- [0013] The optimization of non-aqueous electrolytes can increase energy density, power density and cycle life.
- [0014] US 2001/05485 discloses a gel electrolyte in which a non-aqueous electrolytic solution having a lithium-containing electrolyte salt and dissolved in a non-aqueous solvent is gelled by a matrix polymer. The gelled electrolyte includes a halogen substituted ethylene carbonate obtained by replacing one or more hydrogen atoms in ethylene carbonate by halogens. Since the halogen substituted ethylene carbonate (for instance, fluorinated ethylene carbonate) is low in its reactivity with a negative electrode, the loss of capacity is small so that it is effective for obtaining a better capacity.
- [0015] US 5,830,600 describes fire-retardant electrolyte compositions which comprise a lithium salt dissolved in a fire-retardant solvent selected from the group consisting of phosphates, phospholanes, cyclophosphazenes, silanes, fluorinated carbonates, fluorinated polyethers and mixtures thereof. The conductive compositions formulated are disclosed to be useful in the fabrication of fuel cells, sensors, super capacitors, electrochromic devices and the like.

- [0016] US 5,925,283 describes conductive polymeric gel electrolytes for batteries having high ionic conductivity and sufficiently high solid strength. The ionically conductive polymeric gel electrolyte contains at least a polymer matrix, a non-aqueous electrolytic solution and an electrolytic salt, wherein at least one kind of halogen-substituted carbonic ester is contained as a solvent of the non-aqueous electrolytic solution. Examples for the halogen-substituted carbonic esters given are methyl-2-chloro ethylene carbonate, methyl-2,2,2,-trifluoroethyl carbonate and methyl-2,2,3,3,3-pentafluoropropyl carbonate. Examples of halogen-substituted cyclic carbonic esters given include fluoromethylethylene carbonate, difluoromethylethylene carbonate, trifluoromethylethylene carbonate and other representatives.
- [0017] JP11102727 discloses a method to enhance the safety of a battery by providing an electrolyte consisting of a polymer capable of forming a gelled electrolyte, a non-aqueous solvent, and a lithium salt, and containing at least a halogenated solvent in the solvent mixture for making the gelled electrolyte difficult to burn. Suitable halogenated solvents mentioned include, inter alia, halogenated cyclic carbonates.
- [0018] US 6,743,947 describes electrochemical capacitors, comprising a pair of high surface area electrodes, a separator and an electrolyte, wherein said electrolyte comprises an asymmetric onium salt of a specific structure or a mixture of such salts dissolved in an aprotic, non-aqueous solvent or a mixture of such solvents. According to claim 4 the electrolytic solvent may be selected from carbonates, including halogenated carbonates amongst a greater list of solvents of various chemical structures. No further information concerning the use of halogenated carbonates is given.
- [0019] The optimization of the electrolyte systems in hybrid supercapacitor still offers a significant potential to improve the performance properties of such systems.
- [0020] Accordingly, it has been an object of the present invention to provide hybrid supercapacitor having improved performance properties, in particular lithium hybrid super capacitors having an anode working in a similar (but different way) than lithium batteries.

[0021] These objectives have been achieved by the hybrid super capacitor in accordance with claim 1. Preferred embodiments of the present invention are set forth in the dependent claims and the detailed description hereinafter.

[0022] The electrolyte system in the hybrid supercapacitors according to the present invention comprises an organic solvent or a mixture of organic solvents, said organic solvent or said mixture of organic solvents containing from 0.1 to 100, preferably from 0.1 to 30, more preferably from 0.2 to 20 and particularly preferably from 0.5 to 10 wt%, based on the total weight of the electrolyte organic solvent(s), of a fluorinated carbonate of the general formulae I or II



(II)

[0023] (I)

[0024] wherein R¹ to R⁴, which may be the same or different, are independently selected from hydrogen, fluorine, C₁ to C₈ -alkyl and C₁ to C₈ haloalkyl which the proviso that at least one of R¹ to R⁴ is a fluorine atom or comprises a fluorine atom and R⁵ to R⁶, independently of one another, are selected from hydrogen, C₁ to C₈ alkyl or C₁-C₈ haloalkyl.

[0025] In accordance with the present invention, the electrolyte system of the hybrid supercapacitor may comprise one or more than one fluorinated carbonate. If mixtures of fluorinated carbonates are used, the weight percentages given above are applicable for the entire weight of the mixture of fluorinated carbonates in the electrolyte system.

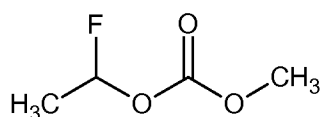
[0026] Generally any fluorinated carbonate of formula I or II is suitable in accordance with the present invention. The skilled person will select the appropriate fluorinated carbonate depending on the other components of the electrolyte system to achieve an optimum combination of properties important for the intended application.

[0027] It may be noted here that fluorinated propylene carbonates (at least one of R¹ to R⁴ is a methyl or a fluorinated methyl group) generally show a

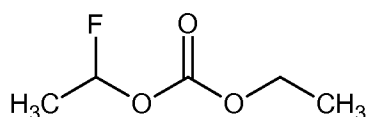
significantly higher viscosity than respective ethylene carbonates. The increased viscosity may lead to a decrease in ion conductivity of the electrolyte system, thus bearing the risk of deterioration of the performance properties of the supercapacitor. Accordingly, it might be advantageous to use as low as possible amounts of fluorinated carbonates in this case or to preferably use fluorinated ethylene carbonates instead of fluorinated propylene carbonates.

[0028] The viscosity also generally increases with increasing number of fluorine atoms in the fluorinated carbonate, which is also a factor the skilled person will take into account.

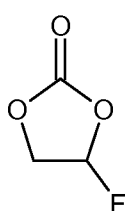
[0029] The following compounds represent preferred representative of fluorinated carbonates which can be used in accordance with the present invention.



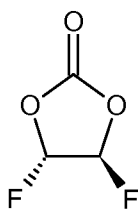
1-Fluoroethyl methyl carbonate



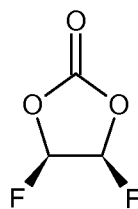
Ethyl-1-Fluoroethyl carbonate



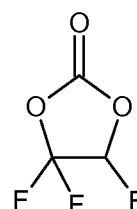
[0030] F1EC



trans-F2EC



cis-F2EC



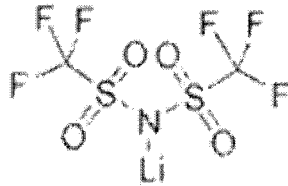
F3EC

[0031] As is apparent for the skilled person, F1EC represents monofluoro ethylene carbonate, F2EC represents difluoro ethylene carbonate and F3EC stands for trifluoro ethylene carbonate.

[0032] Based on the foregoing it is apparent that F1EC, ethyl 1-fluoroethyl carbonate and methyl 1-fluoroethyl carbonate, comprising one fluorine atom in the molecule are particularly preferred when a low viscosity is aimed at.

[0033] Furthermore, non-cyclic carbonates generally are less viscous than cyclic carbonates which may be taken into account by the skilled person.

[0034] In addition to the fluorinated carbonates the electrolyte may comprise 0.1 to 70, preferably 5 to 80 and even more preferably 40 to 60 wt%, based on the total weight of the electrolyte, of LiTFSI



[0035] The electrolyte system in the supercapacitor in accordance with the instant invention in accordance with a preferred embodiment comprises an ester solvent of formula $R\text{-COO-R'}$ or a non-fluorinated carbonate solvent of formula $R\text{-OCOO-R'}$ wherein R and R' independently of one another are selected from $C_1\text{-C}_8$ alkyl or may form a ring system together with the group -COO- or -OCOO- . Preferred examples of this group of solvents are ethyl methyl carbonate, methyl propyl carbonate, dimethyl carbonate, diethyl carbonate, dipropyl carbonate, methyl formate, ethyl acetate, methyl propionate, ethyl propionate, and mixtures of these solvents. The ring system which R and R' may form with the group -COO- or -OCOO- may be $C_1\text{-C}_8$ alkylene; in particular, propylene carbonate may be used. Mixtures of linear and cyclic carbonates may also be used.

[0036] Instead of or in addition to ester or carbonate solvents, the electrolyte system of the hybrid supercapacitor in accordance with the present invention may contain other organic solvents like ethylene glycol dimethyl ether (diglyme), triglyme, tetraglyme, 1,2-dimethoxyethane gamma-butyrolactone, 1,2-ethoxyethane, ethoxymethoxyethane, DMSO, 1,3-dioxolane, formamide, acetoamide, dimethylformamide, acetonitrile, propionitrile, nitromethane, ethylmonoglyme, triester phosphates, trimethoxymethane, THF and derivatives and NMP and derivatives or mixtures thereof to name only some examples.

[0037] The weight of the organic solvent or mixture of organic solvents, based on the total weight of the electrolyte system, is usually of at least 50%, very often of at least 65%, often of at least 75% and may be of 80% or more. On the other hand, it is generally of at most 99%, and it may be of at most 95%, at most 90% or at most 85%.

- [0038] In general the nature of the solvent in the electrolyte system, which is used in combination with the fluorinated carbonate, is not particularly critical and can accordingly be selected by the skilled person depending on the specific situation. The beneficial effect of the fluorinated carbonate, i.e. the improvement of the performance properties of the hybrid supercapacitor is basically independent of the non-fluorinated solvent used.
- [0039] Without being bound to any theory it is assumed that the fluorinated carbonates support the formation of some kind of passivation layer at the anode of the hybrid supercapacitor in accordance with the present invention which may help to prevent the formation of lithium containing dendrites at the anode if the anode contains lithium metal, alloys of lithium or lithium intercalation compounds. Lithium dendrites can grow towards the other electrode of the system and thus bear the risk of creating shortcuts. Furthermore, the cycling performance may be negatively influenced.
- [0040] The electrolyte system of the hybrid supercapacitor in accordance with the present invention generally contains a salt providing the required ionic conductivity.
- [0041] Suitable salts for hybrid supercapacitor are known to the skilled person and described in the prior art so that there is no further detailed description necessary here. The skilled man will select the combination of fluorinated carbonate and other solvent also taking into account that the salt should have a certain solubility in the solvent mixture to provide a sufficient ionic conductivity of the electrolyte system.
- [0042] The hybrid supercapacitor in accordance with the present invention comprises two different electrodes (which is the reason for the term hybrid supercapacitor), one of which works in a similar albeit different way than the anode in lithium batteries. In principle the hybrid supercapacitor in accordance with the present invention combines the energy storage principle of a lithium-ion secondary battery and an electric double-layer capacitor.
- [0043] A capacitive material is characterized by a potential swing during the charge and discharge of the capacitor. The initial output potential

difference of a symmetric cell with capacitive electrodes is 0V and the potentials diverge linearly during charging of cell. By contrast, the battery-like electrode is characterized by an almost constant potential during charging and discharging. Thus, in order to get the largest voltage in an hybrid capacitor, where a capacitive electrode is replaced by a battery-like one, the potential of the selected battery-electrode must be close to the low or high limit of the potential window of the capacitive electrode.

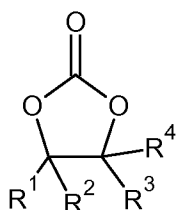
- [0044] Li-intercalation compounds ($\text{Li}_4\text{Ti}_5\text{O}_{12}$, WO_2 , LiCoO_2 , $\text{LiMn}_{1.2}\text{Ni}_{0.5}\text{O}_4$, etc.) have been proposed for electrodes of hybrid capacitors working in organic electrolytes, the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /activated carbon system being one of the more intensively studies systems.
- [0045] The beneficial effect of the fluorinated carbonates as a component of the electrolyte system in the hybrid supercapacitor with one lithium ion based electrode is basically independent of the specific type and nature of the electrodes. Respective electrode materials for hybrid supercapacitor with one electrode based on lithium ions have been described in the literature and are known to the skilled person in a great variety so that an exhaustive description of these electrode materials is neither necessary nor possible here.
- [0046] According to a preferred embodiment of the present invention a graphite negative electrode wherein lithium ions can be intercalated is combined with a porous carbon positive electrode. Respective systems may comprise a positive electrode based on activated carbon and a negative electrode based on graphite or hard carbon and have been described in the literature as Li-ion capacitors.
- [0047] By a so-called pre-doping, i.e. the intercalation of lithium in a graphitic type material prior to the charge/discharge of the capacitor, the potential of the negative electrode can be lowered and the potential window of the positive electrode can be extended. To achieve this, an additional lithium ion source has to be provided and a Li foil has been used for this purpose.
- [0048] Other systems which have been described comprise a positive electrode based on activated carbon and a negative electrode based on non-graphitizable carbon.

- [0049] While the use of metallic lithium has some benefits in improving energy density and cycle life, it also has some drawbacks, in particular from the view point of safety. In view of this it has been proposed to use suitable electrolyte systems where the intercalated lithium can be taken directly from the electrolyte (Béguin et al., J. Power Source 2008, 177, 643) and the electrode systems described therein for the electrodes of the supercapacitor in accordance with the present invention in another preferred embodiment.
- [0050] Hybrid supercapacitors comprising a positive electrode based on activated carbon and comprising at least 20, preferably at least 50 and most preferably at least 80 % activated carbon are preferred.
- [0051] Furthermore, the negative electrode of hybrid supercapacitors in accordance with the present invention is preferably based on graphite and comprises at least 20, preferably at least 50 and more preferably at least 80% of graphite.
- [0052] Generally, the available surface at the electrodes limits the amount of energy which can be stored in the supercapacitor and thus it is advantageous to use electrode materials with high surface areas. The skilled person knows such materials and will select the appropriate combination of electrodes based on his knowledge and the information provided in the prior art.
- [0053] Graphene materials as supercapacitor electrode materials have also been described in the literature and may be used in accordance with another preferred embodiment of the present invention.
- [0054] The electrodes in hybrid supercapacitor are separated by a suitable separator. Suitable materials for such separators are known to the skilled person and have been described in the literature.
- [0055] A preferred material for the separator is based on vinylidene fluoride polymers which are commercially available from Solvay Solexis under the tradename Solef®. Other suitable materials are based on polyolefins.
- [0056] The main role of the separator is to avoid an electrical short cut between the negative and the positive electrode. It may improve electrochemical stability of the system. Furthermore, it can help to control leakage of electrolyte which might detrimentally influence the lifetime of the systems. Furthermore, respective products are easily solution processable and show a good wettability with the electrolyte which is another advantage

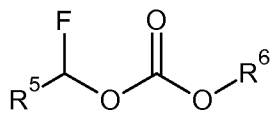
- [0057] The hybrid supercapacitor in accordance with the present invention provides a good combination of energy density, power density and cycle stability, in particular the cycle life time can be improved with the use of fluorinated carbonates as component of the electrolyte system.
- [0058] Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.

Claims

1. A hybrid supercapacitor device comprising at least one positive electrode, at least one negative electrode, a separator and an electrolyte based on one or more organic solvents, wherein the electrolyte comprises from 0.1 to 100 percent by weight, based on the entire weight of the organic solvent(s) in the electrolyte, of at least one fluorinated carbonate of formula I or II



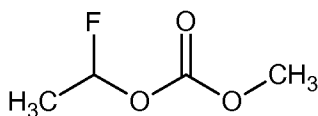
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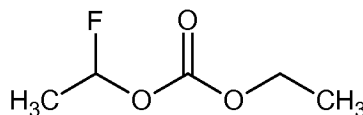
(II)

wherein R¹ to R⁴, which may be the same or different, are independently selected from hydrogen, fluorine, C₁ to C₈ -alkyl and C₁ to C₈ haloalkyl with the proviso that at least one of R¹ to R⁴ is a fluorine atom or comprises a fluorine atom and R⁵ to R⁶, independently of one another, are selected from hydrogen, C₁ to C₈ alkyl or C₁-C₈ haloalkyl.

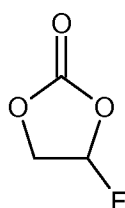
2. The hybrid supercapacitor in accordance with claim 1 wherein the fluorinated carbonate is selected from



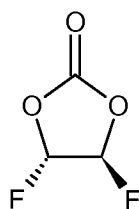
1-Fluoroethyl methyl carbonate



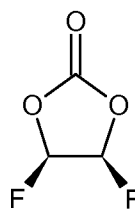
Ethyl-1-Fluoroethyl carbonate



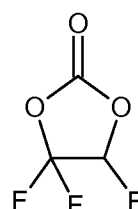
F1EC



trans-F2EC



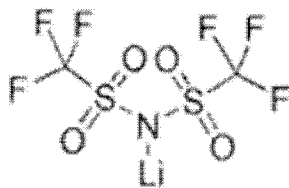
cis-F2EC



F3EC

3. The hybrid supercapacitor in accordance with claim 1 or 2 wherein the content of the at least one fluorinated carbonate ranges from 0.1 to 30 wt% .
4. The hybrid supercapacitor in accordance with claim 3 wherein the content of the at least one fluorinated carbonate ranges from 0.5 to 10 wt%.

5. The hybrid supercapacitor in accordance with any of the preceding claims wherein the electrolyte comprises 0.1 to 70 wt%, based on the entire weight of the electrolyte, of LiTFSI



6. The hybrid supercapacitor in accordance with any of the preceding claims wherein the organic solvent of the electrolyte system comprises an ester solvent of formula $R-COO-R'$ or a non-fluorinated carbonate solvent of formula $R-OCOO-R'$ wherein R and R' independently of one another are selected from C_1-C_8 alkyl or may form a ring system together with the group $-COO-$ or $-OCOO-$.
7. The hybrid supercapacitor in accordance with any of claims 1 to 5 wherein the organic solvent of the electrolyte system comprises a solvent selected from ethyl methyl carbonate, methyl propyl carbonate, dimethyl carbonate, diethyl carbonate, dipropyl carbonate, methyl formate, ethyl acetate, methyl propionate, ethyl propionate, and mixtures thereof.
8. The hybrid supercapacitor in accordance with any of the preceding claims wherein the organic solvent of the electrolyte system comprises a solvent selected from ethylene glycol, dimethyl ether (diglyme), triglyme, tetraglyme, 1,2-dimethoxyethane gamma-butyrolactone, 1,2-ethoxyethane, ethoxy methoxyethane, DMSO, 1,3-dioxolane, formamide, acetoamide, dimethylformamide, acetonitrile, propionitrile, nitromethane, ethylmonoglyme, triester phosphates, trimethoxymethane, THF and derivatives, NMP and derivatives and mixtures thereof.
9. The hybrid supercapacitor in accordance with any of the preceding claims wherein one electrode is an electrode of the lithium battery type.
10. The hybrid supercapacitor in accordance with any of the preceding claims comprising a graphite negative electrode wherein lithium ions can be intercalated and a porous carbon positive electrode.

11. The hybrid supercapacitor in accordance with at least one of claims 1 to 9 comprising a positive electrode based on activated carbon and a negative electrode based on non-graphitizable carbon.
12. The hybrid supercapacitor in accordance with any of the preceding claims comprising a separator based on vinylidene fluoride polymers.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2013/051399

A. CLASSIFICATION OF SUBJECT MATTER

INV. H01G9/022 H01G11/60
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)

H01G C07D H01M H01L

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	DE 197 00 656 A1 (SANYO CHEMICAL IND LTD [JP]) 24 July 1997 (1997-07-24) claims 1-10 the whole document	1-12
X	US 2006/124973 A1 (ARAI JUICHI [JP] ET AL) 15 June 2006 (2006-06-15) the whole document	1-12
Y	US 2009/134353 A1 (KOH MEITEN [JP] ET AL) 28 May 2009 (2009-05-28) the whole document	1-12
Y	EP 0 775 701 A1 (MITSUI PETROCHEMICAL IND [JP]) 28 May 1997 (1997-05-28) the whole document	1-12
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Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

21 March 2013

Date of mailing of the international search report

28/03/2013

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INTERNATIONAL SEARCH REPORT

International application No

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	US 2011/216477 A1 (TAKAHASHI KENZOU [JP] ET AL) 8 September 2011 (2011-09-08) the whole document -----	1-12

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Information on patent family members

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