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(54) Title: ORGANOSILICON GLYCOL-BASED ELECTROLYTES WITH A HYDROXY TERMINUS

(57) Abstract: Disclosed are hydroxy terminated alkylsilane ethers with oligoethylene oxide substituents. They are suitable for use as electrolyte solvents and particularly well suited for use with aqueous environment electrolytic capacitors. Methods for synthesizing these compounds are also disclosed.

ORGANOSILICON GLYCOL-BASED ELECTROLYTES WITH A HYDROXY TERMINUS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority based on U.S. Serial No. 12/770,183 which was filed April 30, 2010.

FEDERALLY SPONSORED RESEARCH/DEVELOPMENT

[0002] This invention was made with United States government support awarded by the following agencies: NSF 0724469. The United States has certain rights in this invention.

BACKGROUND OF THE INVENTION

[0003] The present invention relates to ionic electrolytes useful in connection with electrolytic capacitors and certain other energy storage devices. More particularly it relates to hydroxy terminated organosilicon electrolytes that are particularly useful in an aqueous electrolytic capacitor environment.

[0004] Over the past decade our laboratory has been developing organosilicon based electrolytes for energy storage applications. Various of these organ silicon compounds have low vapor pressure, high flash point, and withstand high operating voltages.

[0005] For example, we previously reported the synthesis of some alkyl terminated trimethylsilyl oligoethylene glycol ethers in L. Zhang et al., Highly Conductive Trimethylsilyl Oligo(ethylene oxide) Electrolytes For Energy Storage Applications, 18 J. Mater. Chem. 3713-3717 (2008). These materials had high ionic conductivity, good electrochemical stability, and good cycling performance when used as electrolyte solvents in lithium-ion cells. However, they were susceptible to being hydrolyzed under some conditions.

[0006] We also reported in U.S. patent application publication 2007/0065728 the concept of placing an alkyl

spacer in such alkyl terminated compounds between the trimethylsilyl group and the remainder of the molecule. This helped the molecule resist hydrolysis. However, the compounds still did not achieve desired performance in certain environments.

[0007] One reason is that a variety of electrolytic capacitors use water to repair aluminum defects. See generally descriptions of electrolytic capacitors in U.S. patent 6,058,006. Conventional aluminum electrolytic capacitors sometimes use an electrolyte mix of gamma-butyrolactone, diethylene glycol, triethylammonium azelaate, and water. To achieve the advantages of our alkyl terminated organosilicon compounds with this type of capacitor there were attempts to replace the gamma-butyrolactone and diethylene glycol with them. However, alkyl terminated organosilicon electrolytes typically had performance issues in this environment.

[0008] In U. Yoon et al., Efficient And Regioselective Photocyclization Reactions Of N-[(ω-Trimethylsilylmethoxy)Polyoxalkyl]Phthalimides To Azacrown Ethers, 41 Heterocycles 2665-2682 (1995) the authors reported the synthesis of $Me_3Si\text{-}CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2\text{-}OH$, $Me_3Si\text{-}CH_2OCH_2CH_2OCH_2CH_2\text{-}OH$ and $Me_3Si\text{-}CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2\text{-}OH$ (and various related compounds) as intermediates in the production of azacrown ethers. Apart from the fact that their syntheses required use of relatively expensive $Me_3Si\text{-}CH_2I$, there was no suggestion in their article to use these intermediates as electrolytes.

[0009] There is therefore a need for additional improvements with respect to organosilicon electrolytes for energy storage devices, particularly improvements relating to compatibility with water environments.

SUMMARY OF THE INVENTION

[0010] In one aspect the invention provides an electrolyte comprising:

[0011] a salt; and

[0012] at least one compound having the following formula:

[0013]

[0014]

[0015] $$R_1\text{-}Si(R_2)(R_3)\text{-}(CH_2)_m(OCH_2CH_2)_n\text{-}OH$$

[0016]

[0017]

[0018] In this compound R_1, R_2 and R_3 are the same or different, and each is selected from the group consisting of alkyl moieties of less than five carbons. Most preferably each of R_1, R_2 and R_3 is CH_3. In any event, both m and n are less than 10, with m and n both most preferably lower than 5, and even more preferably with n equal to 2, 3 or 4.

[0019] One preferred salt for use with such electrolytic capacitors is triethylammonium azelaate, e.g. at less than 2% of the electrolyte. However, alternatively other conventional salts useful with such energy storage devices can be included. See e.g. U.S. patent application publication 2010/0053847 regarding varied salts useful with such capacitors. Various lithium based salts are also known to be compatible with a variety of organosilicon electrolytes.

[0020] Electrolytes can be created with mixtures of multiple such compounds. Alternatively, one of these compounds can be used with other materials (e.g. ethylene glycols; ditrimethyl silane terminated compounds).

[0021] The electrolytes of the present invention are particularly suitable for use in environments where they will be exposed to/mixed with water. For example, aluminum electrolytic capacitors typically add a few

percent of water to their electrolytic solution to help repair the aluminum material.

[0022] In another aspect the invention provides an energy storage device (e.g. an electrolytic capacitor) which has such an electrolyte.

[0023] In yet another form the invention provides methods of producing hydroxy terminated organosilicon compounds having the following formula:

[0024]

[0025]

[0026] $CH_3-Si(CH_3)_2-(CH_2)_mO(CH_2CH_2O)_n-OH$

[0027]

[0028]

[0029] In these compounds m and n are both less than 10, preferably both less than 5. To produce them one reacts $HO(CH_2CH_2O)_r-OH$ with sodium cation, and then reacts the resultant with $Me_3Si(CH_2)_qCl$ and iodide anion. Here, q and r are both less than 10.

[0030] It will be appreciated that the present invention provides electrolytes that are highly useful in energy storage devices where the electrolyte contains or is exposed to water (e.g. especially in aluminum electrolytic capacitors). These electrolytes resist hydrolysis, can be used at relatively high voltages, and have reduced flammability concerns. Note that as n increases the flashpoint of these compounds also increases.

[0031] The present invention also provides improved methods of synthesizing such compounds. In this regard, $Me_3Si(CH_2)I$, a starting material used in prior art syntheses, is undesirably expensive. Its use is avoided by replacing that compound with $Me_3Si(CH_2)Cl$ and catalytic amounts of iodide anion, and adjusting concentrations and reaction conditions to minimize undesired byproducts.

[0032] The above and still other advantages of the present invention will be apparent from the description that follows. It should be appreciated, however, that the following description is merely of the preferred embodiments. The claims should therefore be looked to in order to understand the more comprehensive nature of the claimed invention.

[0033] DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0034] We first describe improved syntheses for producing hydroxy terminated organosilicon compounds having the following formula:

[0035]
[0036]
[0037] $CH_3-Si(CH_3)_2-(CH_2)_mO(CH_2CH_2O)_n-OH$
[0038]
[0039]

[0040] Example 1 - Mixture of 75% $Me_3Si-CH_2OCH_2CH_2OCH_2CH_2-OH$ with about 20% $HO-CH_2CH_2OCH_2CH_2OH$, and about 5% $Me_3Si-CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2-SiMe_3$

[0041] 700mL of diethyleneglycol are mixed with 38g of powdered NaOH and the mixture is stirred under vacuum at 80°C for 4 hours to eliminate most of the water produced in the reaction. After this time the NaOH was essentially completely dissolved and the liquid no longer boiling.

[0042] The temperature was then lowered to 70°C and 21g of NaI was added. Note that increasing the NaI levels above 20% molar equivalent would greatly increase byproducts and cost, and we selected our sodium iodide level lower accordingly.

[0043] Vacuum is no longer needed at this point and the mixture is stirred until all NaI dissolves(about 30 minutes). Then 116 g of chloromethyltrimethylsilane are added, and the mixture is stirred for 3 hours at 70°C and 1 hour at 80°C. After this 200 mL of water are added to

the mixture and it is extracted with hexane (4x300mL), the hexane is evaporated in rotovapor and the compound distilled. This lead to an initial yield of 160g of the 75/20/5 mixture. Interestingly, even this intermediate mixture turned out to have significant utility as an electrolyte.

[0044] Example 2 - $Me_3Si\text{-}CH_2OCH_2CH_2OCH_2CH_2\text{-}OH$

[0045] In order to obtain a higher purity of the Example 2 product, the Example 1 mixture was dissolved in 500mL of water plus 1.5L of methanol and the nonpolar impurities extracted with hexane (2x75mL). The solvent was then evaporated and the remaining compound dissolved in 1.5L of hexane and extracted with water (2x100mL). The solvent was then evaporated. Yield 115mL, 98% pure.

[0046] Example 3 - $Me_3Si\text{-}CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2\text{-}OH$

[0047] 700mL of triethyleneglycol are mixed with 45g of powdered NaOH and the mixture is stirred under vacuum at 90°C for 3 hours to eliminate most of the water produced in the reaction. After this time the NaOH should be completely dissolved and the liquid no longer boiling.

[0048] The temperature is then lowered to 70°C and 24 g of NaI are added. Vacuum is no longer needed and the mixture is stirred until all NaI dissolves (about 30 minutes). Then 135 g of chloromethyltrimethylsilane are added and the mixture is stirred for 3 hours at 70°C and 1 hour at 80°C. After this 70 mL of water are added to the mixture and it is extracted with hexane (3x300mL).

[0049] Half of the solvent is evaporated in rotavapor and 50mL of water are added to extract polar impurities. After that the remaining hexane is evaporated and the Example 3 compound distilled. Yield 180 g, 95% pure.

[0050] Example 4- $Me_3Si\text{-}CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2\text{-}OH$

[0051] 400mL of tetraethyleneglycol are mixed with 18.5g of powdered NaOH and the mixture is stirred under

vacuum at 90°C for 3 hours to eliminate most of the water produced in the reaction. After this time the NaOH should be completely dissolved and the liquid no longer boiling. The temperature is lowered to 70°C and 10.5 g of NaI are added.

[0052] Vacuum is no longer needed and the mixture is stirred until all NaI dissolves (about 30 minutes). Then 56.4 g of chloromethyltrimethylsilane are added and the mixture is stirred for 3 hours at 70°C and 1 hour at 80°C. After this 50 mL of water are added to the mixture and it is extracted with hexane (3x200mL). The solvent is evaporated in rotavapor and the compound distilled. After this 50mL of water are added and 10mL of hexane to extract nonpolar impurities. The water is evaporated in the rotavapor to give the compound. Yield 80 g.

[0053] Once we have a desired electrolyte (or electrolyte mixture) one can add a conventional electrolyte salt, preferably at less than 2%, and use that material in an energy storage device such as an aluminum electrolytic capacitor.

[0054] In addition to compound(s) of the present invention the electrolytes can also have mixed therein various polyethylene glycol compounds and/or a ditrimethyl silane terminated electrolyte.

[0055] Various electrolytes of the present invention have been tested in aluminum electrolytic capacitors. They have been found to resist hydrolysis and to be otherwise compatible with an aqueous environment, while still achieving other desirable properties expected from their alkyl terminated counterparts.

[0056] While various embodiments of the present invention have been described above, the present invention is not limited to just these disclosed examples. There are other modifications that are meant

to be within the scope of the invention and claims. For example, m and n could have larger numbers than the preferred embodiments exemplify.

[0057] Thus, the claims should be looked to in order to judge the full scope of the invention.

[0058] Industrial Applicability

[0059] The present invention provides improved electrolytes, particularly electrolytes suitable for use in aqueous electrolytic capacitor environments. Improved methods for making them are also described.

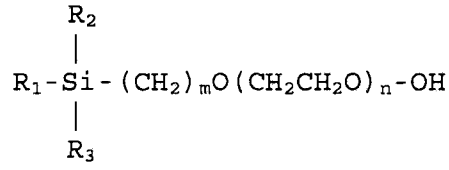
Claims

We claim:

1. An electrolyte comprising:

a salt; and

at least one compound having the following formula:



wherein R_1, R_2 and R_3 are the same or different, and each is selected from the group consisting of alkyl moieties of less than five carbons; and

wherein m and n are both less than 10.

2. The electrolyte of claim 1 wherein each of R_1, R_2 and R_3 is CH_3.

3. The electrolyte of claim 1, wherein m is lower than 5.

4. The electrolyte of claim 1, wherein n is 2 or 3 or 4.

5. The electrolyte of claim 1, further comprising water.

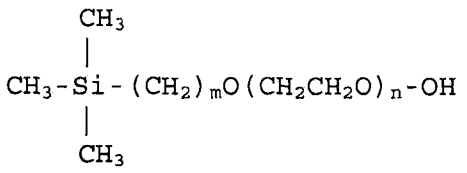
6. The electrolyte of claim 1, further comprising an ethylene glycol.

7. The electrolyte of claim 1, further comprising a ditrimethyl silane terminated electrolyte.

8. The electrolyte of claim 1 positioned in an energy storage device.

9. The electrolyte of claim 8, wherein the energy storage device is an aluminum electrolytic capacitor.

10. A method of producing a compound having the following formula:



wherein m and n are both less than 10;

comprising:

the method comprising:

reacting $HO(CH_2CH_2O)_r$-OH with sodium cation; and

then reacting the resultant with $Me_3Si(CH_2)_qCl$ and iodide anion;

wherein q and r are both less than 10.

11. The method of claim 10, wherein during the reaction the iodide anion is present at no more than 20% of the molarity of $Me_3Si(CH_2)_qCl$.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/030415

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07F7/08 H01G9/035
ADD. H01M6/16 H01M10/052 H01M10/0569

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)
C07F H01G 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 practical, search terms used)
EPO-Internal, WPI Data, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2007 123097 A (SONY CORP.) 17 May 2007 (2007-05-17)	1,3,8
A	abstract	2,4-7, 9-11

A	L. ZHANG ET AL.: "Highly conductive trimethylsilyl oligo(ethylene oxide) electrolytes for energy storage applications", JOURNAL OF MATERIALS CHEMISTRY, vol. 18, no. 31, 9 July 2008 (2008-07-09), pages 3713-3717, XP002641186, DOI: DOI:10.1039/B806290K cited in the application the whole document	1-11

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[X] Further documents are listed in the continuation of Box C.

[X] 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 document 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

Date of the actual completion of the international search	Date of mailing of the international search report
21 June 2011	29/06/2011

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/030415

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2007/065728 A1 (QUALLION L.L.C.) 22 March 2007 (2007-03-22) cited in the application paragraph [0007] - paragraph [0009] paragraph [0090] paragraph [0102] paragraph [0107] claims 1, 21, 22	1-11

A	US 2007/076349 A1 (WISCONSIN ALUMNI RESEARCH FOUNDATION) 5 April 2007 (2007-04-05) paragraph [0018] - paragraph [0020]; figure 4 paragraph [0026] - paragraph [0027] paragraph [0062] - paragraph [0064] example 1 claims 1, 3	1-11

A	US 2003/124432 A1 (DAISO CO., LTD.) 3 July 2003 (2003-07-03) paragraph [0006] - paragraph [0019] examples 1, 2, 4 claims 1, 6	1-11

A	JP 9 025282 A (SHINETSU CHEMICAL CO., LTD.) 28 January 1997 (1997-01-28) abstract	10,11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2011/030415

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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US 2007065728 A1	22-03-2007	NONE	
US 2007076349 A1	05-04-2007	CA 2624188 A1	12-04-2007
		EP 1938346 A2	02-07-2008
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		US 2008273290 A1	06-11-2008
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