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DESCRIPTION

FIELD OF THE INVENTION

[0001] The present invention relates to a coolant composition for a fuel cell, comprising (a) alkylene glycol, (b) deionized water, and (c) a compound containing a trimethylsilyl group.

DESCRIPTION OF THE RELATED ART

[0002] A fuel cell is an engine that produces electricity using electro-chemical reaction of hydrogen and oxygen, and heat is generated incidentally. Scores of KW class stack have been developed to apply fuel cell vehicles for drive system and heat generations per unit volume are increased according to high-capacity of the fuel cell, whereby there has been increasing an importance of the cooling.

[0003] To obtain a required electrical output from a polymer electrolyte fuel cell, the fuel cell is constituted as a cell stack having a construction of many single cells which are connected in series. Ideally, hydrogen as the fuel is converted to electrical energy. Actually, there is some electrical resistance in cell, whereby part of energy is converted to heat energy rather than electrical energy. Since the heat is generated in cell and the cell temperature increases, a cooling plate is inserted several cells for cooling the cell.

[0004] Meanwhile, deionized Water (DI-Water) commonly used in early development stage has high electric resistance and it is excellent in electric insulation and cooling performance. However, DI-water has disadvantages that it is frozen below 0°C and has cold startup of fuel cell vehicles. In addition, there is a problem that ion in the fuel cell system is easily contaminated to decline electronic heat sharply.

[0005] For these reasons, there has been growing interest in the coolant for the fuel cell which is not frozen in the winter and has an excellent electric insulation. Mixture solution of water and alkylene glycols, e.g. monoethyleneglycol and monopropyleneglycol, was used as a coolant for conventional fuel cells.

[0006] However, there was a problem that glycols used in the coolant for conventional fuel cells as main base substance generate an ionic substance to increase electrical conductivity.

[0007] Accordingly, there are needs for antioxidants preventing or delaying the oxidation of main base substance.

[0008] Throughout this application, several patents and publications are referenced and citations are provided in parentheses.

[0009] US5080818 discloses an antifreeze composition comprising water, a glycol and a corrosion inhibitor. It mentions that the glycol is oxidized on contact with air at elevated temperatures and that the oxidation products are corrosive.

[0010] KR2010/0045265 discloses a cooling composition for a fuel cell comprising deionized water, an alkylene glycol and optionally a corrosion inhibitor.

[0011] US4462921 discloses an antifreeze/coolant composition comprising water, a glycol and trimethyl silyl-terminated polycyanopropylmethyl siloxane as a stabilizer for an inorganic silicate corrosion inhibitor.

DETAILED DESCRIPTION OF THIS INVENTION

Technical Purposes of This Invention

[0012] The present inventors have made intensive studies to develop a coolant composition that prevents the oxidation of base, inhibits the generation of an ionic material and maintains antifreezing and low conductivity. As a result, the present inventors have prepared the present invention in such a manner that a compound containing a trimethylsilyl group is added with alkylene glycol contained in antifreezing coolant compositions for conventional fuel cell vehicles. They have found that the present composition has not only anti-freezing potency being similar to or higher than conventional compositions but also plausible anti-oxidation potency to alkylene glycols to prevent the increase in electrical conductivity value which is an important property in coolants for fuel cells.

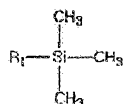
[0013] Accordingly, it is an object of this invention to provide a coolant composition for a fuel cell.

[0014] Other objects and advantages of the present invention will become apparent from the detailed description to follow taken in conjunction with the appended claims and drawings.

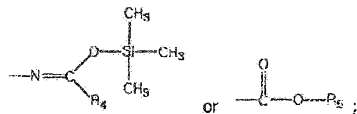
Technical Solutions of This Invention

[0015] In one aspect of the present invention, there is provided a coolant composition for a fuel cell, comprising (a) alkylene glycol, (b) deionized water and (c) a compound represented by the following Formula I:

[Formula I]



wherein R_1 is halo, C_{1-10} alkyl, $-NR_2R_3$, azide, C_{1-10} alkaneamide,



each of R_2 , R_3 , R_4 , and R_5 is independently oxygen or C_{1-10} alkyl.

[0016] The present inventors have made intensive studies to develop a coolant composition that prevents the oxidation of base, inhibits the generation of an ionic material and maintains antifreezing and low conductivity. As a result, the present inventors have prepared the present invention in such a manner that a compound containing a trimethylsilyl group is added with alkylene glycol contained in antifreezing coolant compositions for conventional fuel cell vehicles. They have found that the present composition has not only anti-freezing potency being similar to or higher than conventional compositions but also plausible anti-oxidation potency to alkylene glycols to prevent the increase in electrical conductivity value which is an important property in coolants for fuel cells.

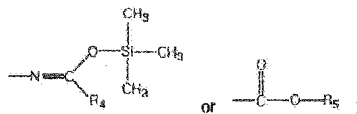
[0017] According to a preferred embodiment, alkylene glycol of the present invention is selected from the group consisting of monoethyleneglycol, monopropyleneglycol, diethyleneglycol, dipropyleneglycol, glycerin, triethyleneglycol and tripropyleneglycol, more preferably monoethyleneglycol, monopropyleneglycol, diethyleneglycol, dipropyleneglycol or glycerin, and most preferably monoethyleneglycol or monopropyleneglycol.

[0018] The DI-water (deionized Water) used in the present invention is DI-water deionized by ion exchange, pure distilled water or distilled water which is distilled twice.

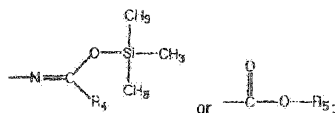
[0019] The compound contained in the present coolant composition for fuel cells has trimethylsilyl group as a structural nucleus represented by the Formula I. As used herein, the term "halo" used to define the Formula I of the compound of the present invention refers to a halogen element and includes, for example, fluoro, chloro, bromo and iodo, more preferably fluoro, chloro or bromo. The term " C_1 - C_{10} alkyl" refers to a linear or branched, saturated hydrocarbon group and includes, for example, methyl, ethyl, *n*-propyl, isopropyl, isobutyl, propyl, *n*-butyl, *t*-butyl, *n*-hexyl, *n*-octyl and *t*-octyl.

[0020] The term " C_{1-10} alkaneamide" refers to a compound in which an amide group is linked to an alkyl group of 1-10 carbons.

[0021] According to a preferred embodiment, R_1 in the present invention is halo, C_{1-5} alkyl, $-NR_2R_3$, azide, C_{1-5} alkaneamide,



each of R_2 , R_3 , R_4 , and R_5 is independently oxygen or C_{1-5} alkyl, more preferably R_1 is halo, C_{1-3} alkyl, $-NR_2R_3$, azide, C_{1-3} alkaneamide,



each of R_2 , R_3 , R_4 , and R_5 is independently oxygen or C_{1-3} alkyl.

[0022] According to a preferred embodiment, the compound of the present invention is trimethylsilyl bromide; trimethylsilyl chloride; trimethylsilyl azide; trimethylsilyl methylester; trimethylsilyl amine; trimethylsilyl dimethylamine; trimethylsilyl diethylamine; N- trimethylsilyl acetamide; or N,O-bis(trimethylsilyl) acetamide. Most preferably the compound is N,O-bis(trimethylsilyl) acetamide or N- trimethylsilyl acetamide.

[0023] The compound represented by the Formula I in the present invention prevents the oxidation of alkylene glycol which is base, thereby inhibiting the generation of an ionic material. As a result, it represents the characteristics that the increase rate of change of electrical conductivity is low and the initial conductivity is maintained over the long term in which is the most important feature of the present invention.

[0024] According to a preferred embodiment, the present composition comprises 30-60% by weight of alkylene glycol, 35-65% by weight of deionized water and 0.001-5% by weight of the compound represented by the Formula I based on the total weight of the composition. More preferably, the composition comprises 40-55% by weight of alkylene glycol, 42-59.99% by weight of deionized water and 0.01-3% by weight of the compound represented by the Formula I based on the total weight of the composition.

[0025] Where the composition of the present invention comprises 30-60% by weight of alkylene glycol, 35-65% by weight of deionized water and 0.001-5% by weight of the compound represented by the Formula I based on the total weight of the composition, it determines an excellent effect that the compound represented by the Formula I prevents the oxidation of alkylene glycol to keep the fluctuation rate of electrical conductivity low level.

[0026] According to a preferred embodiment, the compound of the present invention prevents the oxidation of alkylene glycol to keep the fluctuation rate of electrical conductivity (post-oxidation conductivity/initial conductivity) below 40-folds, and more preferably 3 to 40-folds.

[0027] According to a preferred embodiment, the compound of the present invention prevents the oxidation of alkylene glycol to keep the fluctuation rate of electrical conductivity for graphite-based bipolar plate (post-oxidation conductivity/initial conductivity) below 40-folds, and more preferably 5 to 40-folds.

[0028] According to a preferred embodiment, the compound of the present invention prevents the oxidation of alkylene glycol to keep the fluctuation rate of electrical conductivity for aluminum test piece (post-oxidation conductivity/initial conductivity) below 20-folds, and more preferably 3 to 20-folds.

[0029] The compound of the present invention can be used as a coolant for a cooling system of a fuel cell driving device at below 40 $\mu\text{S}/\text{cm}$ of an electrical conductivity, and more preferably 9-40 $\mu\text{S}/\text{cm}$.

[0030] According to a preferred embodiment, the amount of acid generated after oxidation of alkylene glycol in the composition of the present invention is no more than 700 ppm, and more preferably the amount of acid generated after oxidation for graphite-based bipolar plate is 150-700 ppm and the amount of acid generated after oxidation for aluminum test piece is 20-160 ppm.

[0031] The antifreezing coolant composition of the present invention may include pH regulators, dyes, antifoaming agents, or corrosion inhibitors. The corrosion inhibitors may include a variety of corrosion inhibitors known in the art within the range that does not affect the electrical conductivity of the antifreezing coolant composition of the present invention, for example, carboxylate, phosphate, nitrate, nitrite, molybdate, tungstate, borate, silicate, sulfate, sulfite, carbonate, amine salts, triazole and thiazole.

Effects of This Invention

[0032] The features and advantages of the present invention will be summarized as follows:

1. (i) The present invention provides a coolant composition for a fuel cell, comprising (a) alkylene glycol, (b) deionized water, and (c) a compound containing a trimethylsilyl group represented by the Formula I.
2. (ii) The compound containing a trimethylsilyl group of the composition in the present invention prevents the oxidation of alkylene glycol, whereby the generation of an acid is no more than 700 ppm.
3. (iii) Additionally, the compound prevents the oxidation of alkylene glycol to inhibit the generation of an ionic material, whereby there is an effect that reduces the increase fluctuation rate of electrical conductivity.
4. (iv) Therefore, the coolant composition for a fuel cell of the present invention may be used as a coolant for a cooling system of a fuel cell driving device with below 40 $\mu\text{s/cm}$ of an electrical conductivity even without being frozen in the winter.

EXAMPLES OF THE INVENTION

[0033] The present invention will now be described in further detail by examples. It would be obvious to those skilled in the art that these examples are intended to be more concretely illustrative and the scope of the present invention as set forth in the appended claims is not limited to or by the examples.

EXAMPLES

Preparation Example: Preparation of antifreezing coolant composition

[0034] Amounts of ingredients described as Table 1 were weighed using balance, added to DI-water and stirred until the mixture was became an homogeneous solution to prepare a antifreezing coolant composition. DI-water which is removed ions by water purification system was used in the present invention. Glycols such as ethyleneglycol were purchased from DOW Chemical. N,O-bis(trimethylsilyl)acetamide was purchased from Lancaster. Tocopherol, xylitol, and N, N-dimethylacetamide were purchased from JUNSEI. N-trimethylsilylacetamide was purchased from Acros Organics.

[Table 1]

[illegible]

content of antifreezing coolant composition									
Content (Weight %)	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Comparative Example 1	Comparative Example 2	Comparative Example 3
bis(trimethylsilyl) acetamide	0.01	0.05	0.1	0.2	1	-	-	-	-
Tocopherol	-	-	-	-	-	-	-	0.01	-
xylitol	-	-	-	-	-	-	-	-	0.2
N-trimethylsilyl acetamide	-	-	-	-	-	0.01	-	-	-
total	100	100	100	100	100	100	100	100	100

Experimental Example 1: Measurement on electrical conductivity and amounts of an acid generation after oxidation for a antifreezing coolant composition

[0035] An acid was generated by thermal oxidation of alkylene glycol to increase electrical conductivity. Thermal oxidation test was subject to measure the fluctuation of electrical conductivity and the generation amount of an acid before/after oxidation for antifreezing coolant composition. To promote oxidation, a component used in fuel cell cooling system was placed in an airtight container made with Teflon material. 180 ml of antifreezing coolant composition was added into the component. The airtight container was blocked and left for 500 hours at 100°C oven. Electrical conductivities and generation amounts of an acid before/after test were measured using Thermo orion 162A conductivity meter and ion chromatography (IC).

[0036] A graphite-based bipolar plate as a non-metallic material among fuel cell system components (width 2 cm x height 2 cm) and a test piece of Al 2000-based as metallic material were used for the test and the results of test were represented in Table 2 and Table 3:

[Table 2]

Thermal oxidation test of antifreezing coolant composition for graphite-based bipolar plate										
		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Comparative Example 1	Comparative Example 2	Comparative (Example 3)
fluctuation of electrical conductivity (μs/cm)	initial	0.53	1.14	2.21	2.50	7.50	0.25	0.33	0.27	0.62
	post-oxidation	20.49	15.01	24.37	27.14	37.27	9.21	65	54	68
	fluctuation rate of electrical conductivity (post-oxidation conductivity/initial conductivity)	38.7	13.2	11	10.9	5	36.8	197	200	110
generation amounts of an acid (ppm)	initial	0	0	0	0	0	0	0	0	0
	post-oxidation	157	135	201	239	347	657	1300	1239	2816

[0037] As shown in Table 2, it was determined that both the amount of the acid generation and the fluctuation rate of the electrical conductivity after oxidation for graphite-based bipolar plate in Examples 1 to 6 were less than those in Comparative Examples 1 to 3. Therefore, it would be appreciated that N,O-bis(trimethylsilyl)acetamide including trimethylsilyl group and trimethylsilylacetamide were prevent the oxidation of ethyleneglycol as a base to keep the fluctuation rate of electrical conductivity (post-oxidation conductivity/initial conductivity) low level

[Table 3]

Thermal oxidation test of antifreezing coolant composition for test piece of Al 2000-based										
		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Comparative Example 1	Comparative Example 2	Comparative Example 3
fluctuation of electrical conductivity (μs/cm)	initial	0.53	1.14	2.21	2.50	7.50	0.45	0.33	0.27	0.62
	post-oxidation	9.98	9.81	14.23	18.31	27.51	8.81	10.28	15.38	18.57
	fluctuation rate of electrical conductivity (post-oxidation conductivity/initial conductivity)	18.8	8.6	6.4	7.3	3.7	19.5	31.2	57	30

Thermal oxidation test of antifreezing coolant composition for test piece of Al 2000-based										
		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Comparative Example 1	Comparative Example 2	Comparative Example 3
generation amounts of an acid (ppm)	initial	0	0	0	0	0	0	0	0	0
	post-oxidation	29	20	41	49	71	152	216	324	287

Experimental Example 2: Measurement on freezing temperature for antifreezing coolant composition

[0038] A freezing temperature for antifreezing coolant composition in the Example 1 was measured by KS M 2142. Briefly, the processes were as follow: first, acetone or methanol were put into cooling tank and added slowly dry ice to make coolant. 75-100 ml of the resultant was put into cooling tube to measure the freezing temperature using a thermometer. The end of the thermometer was placed in the center of the antifreezing coolant composition of interest for analysis. The results of measurement were represented in Table 4:

[Table 4]

Freezing temperature for antifreezing coolant composition in the Example 3	
sample [Example 3 : DI-water]	freezing temperature (°C)
50 : 50	-34.7
40 : 60	-22.1
30 : 70	-13.3
20 : 80	-7.2
10 : 90	-3.1

[0039] As shown in Table 3, even though the antifreezing coolant composition in Example 3 was diluted with DI-water at certain weight ratios, its freezing temperature was measured to be maintained at below 0°C.

REFERENCES CITED IN THE DESCRIPTION

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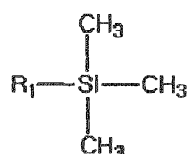
Patent documents cited in the description

- [US5080818A \[0009\]](#)
- [KR20100045265 \[0010\]](#)
- [US4462921A \[0011\]](#)

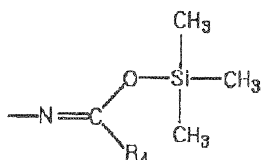
PATENTKRAV

1. Kølemiddelsammensætning til en brændselscelle, omfattende (a) alkylen-
glycol, (b) afioniseret vand og (c) en forbindelse repræsenteret af følgende formel
I:

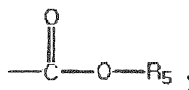
[Formel I]



hvor R₁ er halogen, C₁₋₁₀ alkyl, -NR₂R₃, azid, C₁₋₁₀ alkanamid,



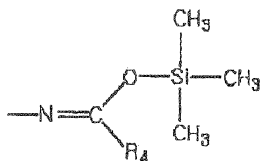
eller



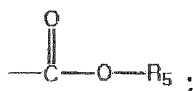
hver af R₂, R₃, R₄ og R₅ uafhængigt er oxygen eller C₁₋₁₀ alkyl.

2. Sammensætning ifølge krav 1, hvor alkylenglycol er valgt blandt gruppen
bestående af monoethylenglycol, monopropylenglycol, diethylenglycol, dipro-
pylenglycol, glycerin, triethylenglycol og tripropylenglycol.

3. Sammensætning ifølge krav 1, hvor R₁ er halogen, C₁₋₅ alkyl, -NR₂R₃, azid,
C₁₋₅ alkanamid,

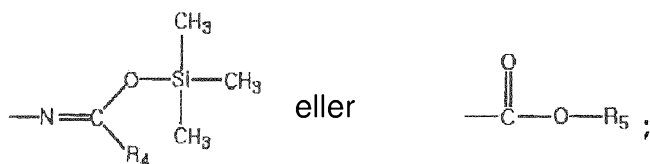


eller



hver af R₂, R₃, R₄ og R₅ uafhængigt er oxygen eller C₁₋₅ alkyl.

4. Sammensætning ifølge krav 3, hvor R_1 er halogen, C_{1-3} alkyl, $-NR_2R_3$, azid, C_{1-3} alkanamid,



hver af R_2 , R_3 , R_4 og R_5 uafhængigt er oxygen eller C_{1-3} alkyl.

5. Sammensætning ifølge krav 4, hvor forbindelsen er trimethylsilylbromid; trimethylsilylchlorid; trimethylsilylazid; trimethylsilylmethyester; trimethylsilylamin; trimethylsilyldimethylamin; trimethylsilyldiethylamin; N-trimethylsilylacetamid; eller N,O-bis(trimethylsilyl)acetamid.

6. Sammensætning ifølge krav 5, hvor forbindelsen er N,O-bis(trimethylsilyl)-acetamid eller N-trimethylsilylacetamid.

7. Sammensætning ifølge krav 1, hvor sammensætningen omfatter 30-60 vægt-% alkylenglycol, 35-65 vægt-% afioniseret vand og 0,001-5 vægt-% af forbindelsen repræsenteret af formel p I baseret på sammensætningens samlede vægt.

8. Sammensætning ifølge krav 1, hvor forbindelsen forhindrer oxidering af alkylenglycol for at holde fluktuationsraten af elektrisk ledeevne (post-oxiderings-ledeevne/indledende ledeevne) under 40 gange.

9. Sammensætning ifølge krav 8, hvor forbindelsen forhindrer oxidering af alkylenglycol for at holde fluktuationsraten af elektrisk ledeevne for grafitbaseret bipolar plade (post-oxidationsledeevne/indledende ledeevne) under 40 gange.

10. Sammensætning ifølge krav 8, hvor forbindelsen forhindrer oxidering af alkylenglycol for at holde fluktuationsraten af elektrisk ledeevne for aluminium (post-oxideringsledeevne/indledende ledeevne) under 20 gange.