

Development of Fuel Cell Coolant

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ABSTRACT

Since fuel cell coolant (FC coolant) should have insulating properties for the purpose of electric leakage prevention, ion-exchange resin is used in the system to remove ions from the coolant. An antioxidant appropriate for FC coolant was formulated for the developed coolant, thereby enhancing oxidation resistance and reducing the generated ion content. This enabled a 40% reduction in the amount of ion-exchange resin.

1. Introduction

Fuel cell vehicles are attracting attention as zero emission automobiles because they do not generate CO₂ when they run. However, the fuel cell (FC) stacks that generate their power also generate heat together with electricity, so they require cooling with coolant. The coolant requires insulating properties in order to help prevent electric leakage, and while the FC generates power, those insulating properties are maintained by ion-exchange resin that is built into the system for the purpose of removing ions from the coolant. Figure 1 shows the layout of the ion-exchange resin in the FC cooling system.

When ethylene glycol (EG), which is generally used as a coolant base material in internal combustion engines, is used as the FC coolant base material, the non-freezing property of EG can be assured, but oxidation results in ionic material being produced. Therefore, the system needs large amounts of ion-exchange resin to be loaded

in order to remove the ionic material from the coolant.

The present development project addressed the need for lighter weight components in fuel cell vehicle. An FC coolant that minimizes the production of oxidants generated from the coolant was developed with the goal of reducing the amount of ion-exchange resin installed in the system.

2. Development Goals

The development of FC coolant that would enable reduction of the amount of ion-exchange resin first required enhanced oxidation resistance and reduced production of ionic material. It was also necessary that the FC coolant not promote the release of ions from the material composing the cooling system parts nor alter the physical properties of that material to any great extent. It is further necessary to assure its cooling performance as well as its non-freezing property at low temperatures for use in cold regions. The objectives of this development project were therefore set forth as follows:

- (1) Enhanced oxidation resistance
Enhance oxidation resistance with regard to EG and reduce the production of ionic material due to oxidation by 90% or more.
- (2) Limited elution of ions from the cooling system material
Limit ion release from material used in the cooling system to the same level as that from EG in an aqueous solution.
- (3) Compatibility with cooling material
Limit changes in volume and other physical properties with respect to material used in the cooling system to the same level as EG in aqueous solution.
- (4) Cooling performance as well as non-freezing property in cold regions

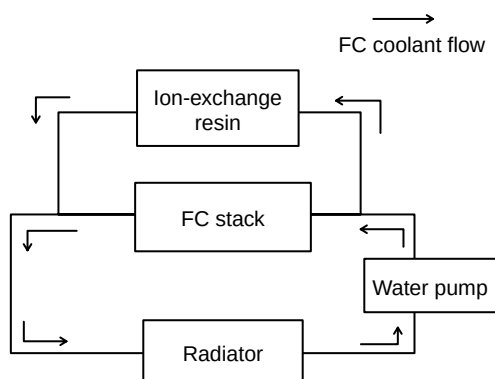


Fig. 1 Ion-exchange resin layout in FC cooling system

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The cooling performance and non-freezing property are physical properties of the mixed solvent composed of the base materials and water, and these properties are to be equivalent to EG in an aqueous solution.

3. Method of Addressing Goals

In order to obtain the needed cooling performance, the base materials were studied. In order to enhance the oxidation resistance, a study of additives was conducted.

3.1. Selection of Base Materials

Table 1 shows the main properties of commonly used base materials, in this case, EG, water, alcohols, glycols (other than EG), glycol ethers, and hydrocarbon. These base materials are compared with EG in terms of specific heat, viscosity, and melting point. Water is superior in specific heat and viscosity but has a high melting point that makes it inferior in non-freezing properties. Although the alcohols, ethers, and hydrocarbon are superior in viscosity and melting point, they have low specific heat so their cooling properties are inferior. Consequently, there are no base materials with physical properties that make them superior to EG in terms of specific heat, viscosity, and melting point. EG was therefore selected as a base material that would enable a balance between cooling and non-freezing properties.

3.2. Investigation of Additives

3.2.1. EG oxidation reaction

Figure 2 shows the oxidation reaction undergone by EG in aqueous solution containing dissolved oxygen. In general, primary alcohols possessing hydroxy groups undergo oxidation reactions that proceed through radical reactions to aldehyde and then to carboxylic acid. The oxidation reaction proceeds similarly in EG, ultimately producing acids such as glycolic acid and formic acid⁽¹⁾.

Figure 3 shows the adsorption of glycolic acid and formic acid from among the ions adsorbed by ion-exchange resin in the FC cooling system during power generation. Extending the duration of power generation by the FC tends to cause more formic acid and glycolic acid ions to be adsorbed by the ion-exchange resin. This indicates that the glycolic acid and formic acid produced by the oxidation of EG in the FC cooling system has been adsorbed when passing the ion-exchange resin.

3.2.2. Criteria for selection of antioxidant

Methods for inhibiting the oxidation of EG include:

- (1) Inhibit progression of the reaction by radical-scavenging
- (2) Reduce the environmental temperature
- (3) Remove dissolved oxygen

Of these, items (2) regarding temperature and (3) regarding removal of oxygen are determined by the system environment. This makes it challenging to address these factors from the coolant side. Investigation was therefore

Table 1 Performance of base materials

Base material	Specific heat	Viscosity	-- -- + ++ Good
			Melting point
EG	+	+	+
Water	++	++	-
Alcohol	-	++	++
Glycol (except EG)	-	-	-
Glycol ether	-	++	++
Hydrocarbon	--	++	+

directed to antioxidants with radical-scavenging and deoxygenation properties.

The selection of an antioxidant also involves two required criteria on the system side in addition to prevention of oxidation. One is heat resistance. The antioxidant should perform its role even in high temperature regions. The other is that it should have nonionic properties so that it will not be removed by the ion-exchange resin installed inside the passages.

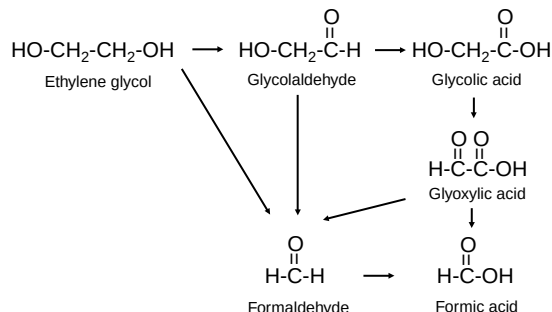


Fig. 2 Oxidation reaction of ethylene glycol

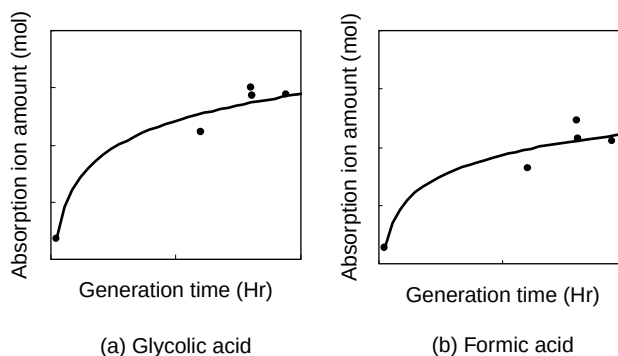


Fig. 3 Adsorption ion on ion-exchange resin (glycolic acid and formic acid)

Table 2 Performance of antioxidants

	Antioxidant	Heat resistance	Ionic
Nitrogen-containing compounds	#1	++	Ionic
	#2	++	Ionic
	#3	++	Ionic
Hydroxy compounds	#4	-	Non ionic
	#5	++	Non ionic
	#6	++	Ionic
	#7	++	Non ionic
	#8	+	Ionic

-- - + ++
Good

3.2.3. Results of antioxidant selection

Various antioxidants with the nitrogen-containing compounds and hydroxy compounds like those numbered 1 to 8 in Table 2 were selected according to the above criteria. Numbers 5 and 7 in the hydroxy group were selected as satisfying the conditions of heat resistance and nonionic property. These were designated antioxidants A and B.

3.2.4. Predicting the antioxidant reaction mechanism

In general, the following types of reaction provide anti-oxidation performance in antioxidants that possess hydroxy groups⁽²⁾:



As in Eq. (1), the antioxidant AO-H provides the hydroxy group hydrogen atom $H^{\cdot}$, and the antioxidant radical $AO^{\cdot}$ captures the various radicals generated by the reaction system. Figure 4 shows one example of the antioxidant reaction mechanism that is conjectured to operate in EG oxidation⁽³⁾. First, one of the EG hydroxy groups is attacked by hydroxyl radicals or other such radicals that pull away the hydrogen atom $H^{\cdot}$, turning the group into an alcoxyl radical. That then reacts with oxygen in the passageway to form glycoaldehyde. When that oxidation reaction occurs, the hydrogen atom provided by the antioxidant captures the hydroxyl radicals, alcoxyl

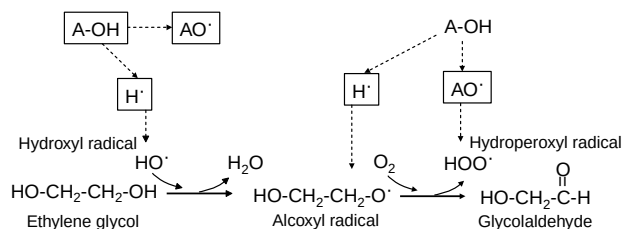


Fig. 4 Oxidation inhibition mechanism of EG by antioxidant

radicals, hydroperoxyl radicals, and the like to stabilize them, and the remainder antioxidant radical $AO^{\cdot}$ captures them as well.

There are also antioxidants that possess deoxygenation properties. An example of such a reaction is shown in Eq. (2).



The rate of the oxidation reaction is also affected to a large extent by the oxygen concentration. The deoxygenation function can therefore slow down the oxidation reaction rate.

4. Results of Performance Evaluation

4.1. Results of Oxidation Resistance Evaluation

The FC coolant was made from the selected base materials and antioxidant, and its oxidation resistance performance was evaluated by means of component heat-resistance testing. The dilution concentration of the base materials, EG, was set at 50%. Antioxidant A or B was added to make FC coolant A and FC coolant B. Their evaluation temperature was set at 100°C and their oxidation resistance was compared to that of the EG aqueous solution. Figure 5 shows the results.

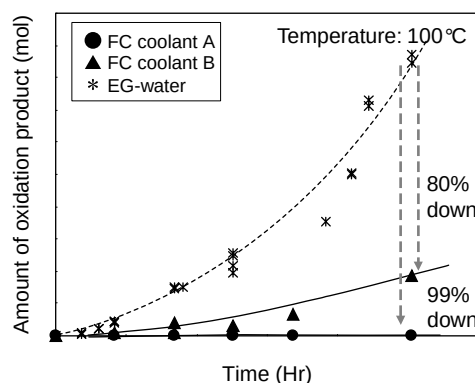


Fig. 5 Oxidation resistance test result

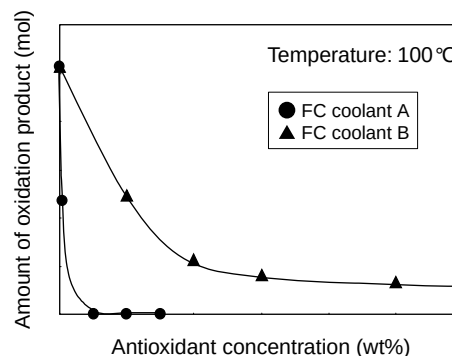


Fig. 6 Effect of antioxidant concentration for oxidation resistance

The EG aqueous solution to which they were compared showed an increase in oxidation product as the test time increased. However, the amount of oxidation product was held down in the FC coolant formulated with antioxidant, with FC coolant A showing a reduction in oxidation production of 99% or more, and FC coolant B a reduction of approximately 80%.

Figure 6 shows the amount of oxidation product with varying concentrations of antioxidant. The amount of oxidation product can be reduced by increasing the antioxidant concentration. In the case of FC coolant A, in particular, adding antioxidant to a certain concentration or greater brought the amount of oxidation product more or less to zero, providing sufficient anti-oxidation performance.

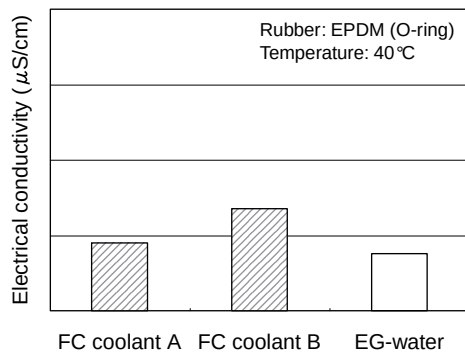


Fig. 7 Coolant extraction performance for rubber

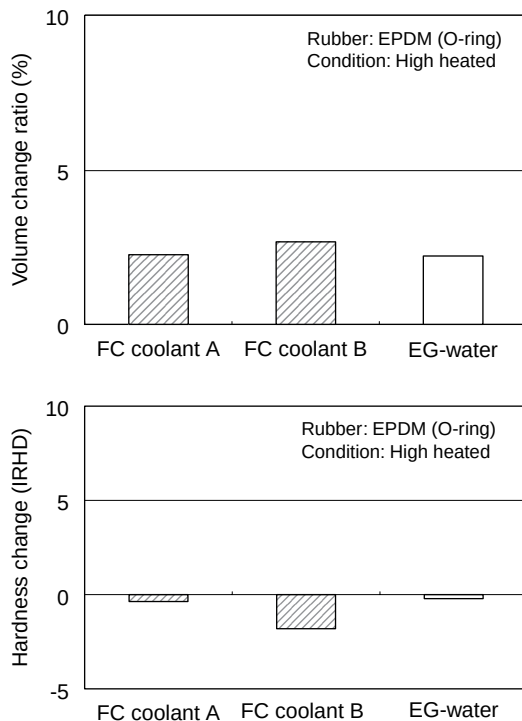


Fig. 8 Coolant application performance for rubber

4.2. Results from Verification of Material Elution

As explained above, it is important that the insulating properties of the FC coolant be maintained. Therefore, the elution of ionic material from the material composing the passages should not be promoted. An evaluation was therefore carried out of elution in the rubber and resin materials from which cooling system parts are made. The quantity of ions eluted by immersion of the material was evaluated in terms of changes in the conductivity of the coolant. It was confirmed that with both the rubber and resin materials, the conductivity of the FC coolant was equivalent to that of the EG aqueous solution. Figure 7 shows ion elution results from rubber material as an example of this.

4.3. Results from Confirmation of Material Compatibility

In order to confirm the influence of the physical properties of the material from which the passageways are made, the rubber and resin materials were subjected to testing for material compatibility similar to the testing for elution. The rubber material was measured for changes in volume, hardness, tensile strength, and elongation before and after immersion. The resin material was measured for changes in flexural strength and flexural modulus. Both the rubber and resin materials showed rates of change with FC coolant that were equivalent to those with EG aqueous solution, confirming that their material compatibility is equivalent to the EG aqueous solution. Figure 8 shows an example of the material compatibility results for rubber material.

5. Ion-exchange Resin Reduction Effect

The effect of reduction in the amount of ion-exchange resin by enhancing oxidation resistance in the FC coolant was estimated with regard to FC coolant A, in particular, which has superior oxidation resistance. The results are shown in Fig. 9. Enhancement of the FC coolant oxidation resistance reduced the adsorption of ionic material due to oxidation of the FC coolant. As a result,

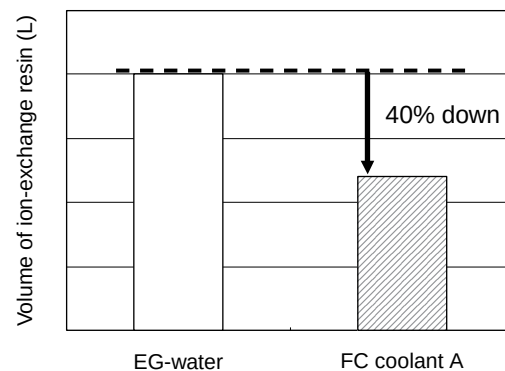


Fig. 9 Reduction of ion-exchange resin through FC coolant

the amount of ion-exchange resin installed in the vehicle could be reduced by 40%, for a saving of weight in parts.

6. Conclusion

- (1) As an effect of adding antioxidant, an FC coolant was developed that reduced the ionic product due to oxidation 90% or more relative to EG.
- (2) It was confirmed that this coolant has compatibility with cooling system parts equivalent to that of EG.
- (3) Adoption of this coolant for use enabled a 40% reduction in the amount of ion-exchange resin.

References

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