

Dielectric study of water/methanol mixtures for use in pulsed-power water capacitors

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Large pulsed-power systems normally use a solid capacitive primary storage and a water capacitor for secondary storage. It is shown that the electrical breakdown strength is increased and the maximum storage time is enhanced from the microsecond level to the millisecond level when the water is replaced by a water/methanol mixture. The increased time scale in the second storage enables the use of an inductive primary storage. The mixing of methanol in the water decreases the relative permittivity. However, due to the increased electrical breakdown strength, a higher energy density is nevertheless possible. Previous work with water/ethylene glycol has manifested the problem of charge injection that occurs when energy is stored for millisecond time scales at high electrical stress. Water/methanol mixtures show less tendency for charge injection and a better ability to store energy at millisecond time scales. © 2003 American Institute of Physics. [DOI: 10.1063/1.1544644]

I. INTRODUCTION

The need for high-power pulses has been growing since the 1960s, and among the applications are electromagnetic pulse testing, inertial confinement fusion,^{1,2} lightning simulation, and laser excitation.³ The short time, typically around 100 ns, peak power levels for these pulses range from megawatts to terawatts. A generator used to produce these powers usually consists of an intermediate storage, with water as a dielectric medium, that is pulsed-charged by a Marx generator and then discharged through a pulse forming line (PFL) into the load.⁴ Water is used as a dielectric because of its high permittivity (ϵ), and for commercial purposes it has the benefit of being cheap and environmentally friendly. Oil is also frequently used as a dielectric and for insulation in high-voltage, pulsed-power systems,³ this is mainly due to the high dielectric breakdown strength acquired. Liquid dielectrics have advantages over solids in that they can be circulated (making repairs of breakdown faults automatic) and are practically suited to applications involving complex geometries. A water dielectric PFL, called a water transmission line, makes use of the high ϵ of water and thus minimizes the overall size of the system.

A Marx generator as primary storage enables the necessary microsecond-long charge time of the intermediate capacitive storage, required when using pure water as dielectric. However, for large pulse generators, it would be desirable to replace the Marx generator (capacitive energy storage) with a superconducting coil (inductive energy storage), as it is a more efficient way of storing energy. This seems even more interesting when considering the new metallic superconductive material MgB₂.^{5,6} Such an inductive primary storage needs a few milliseconds to discharge, which presupposes an intermediate storage capability in the

same range. Highly purified water is conductive due to the auto-ionization process⁷



and at temperatures above 0 °C pure water shows insufficient insulating capability. To prolong the intermediate storage capability an antifreeze is added, enabling temperature reduction below 0 °C, which slows the auto-ionization process and thereby diminishes the conductivity.³ This article focuses on the effects of storage time, charge injection, and energy density when using a water/methanol mixture as a dielectric medium in an intermediate storage capacitor.

Water and water/ethylene glycol mixtures of different concentrations have previously been studied with respect to storage time, relative permittivity, dielectric strength, and charge injection.^{3,4,8} The relative permittivity for interesting water/alcohol mixtures decreases with increasing concentration of alcohol, but increases with decreasing temperature.^{9,10}

The effect of charge injection becomes important as the intermediate storage time is prolonged from microseconds to milliseconds. Water molecules are ionized when the electrodes are charged, causing charge injection to occur at the surface of the electrodes. These ions will, since there is an electric field present, start moving towards the other electrode. When reaching the other electrode, the ions are neutralized. This leads to an unwanted conductivity that depends on the mobility μ of the injected ion, the electric field, and the intrinsic time constant τ of the capacitor (without charge injection).¹¹⁻¹⁴ Investigations and measurements show that for a water/ethylene glycol mixture, the mobility of the injected ions is similar to the mobility of the H⁺ ion.^{8,15-17}

The drift speed ν for an ion in an electric field E is given by

$$\nu = \mu E [\text{m/s}], \quad (2)$$

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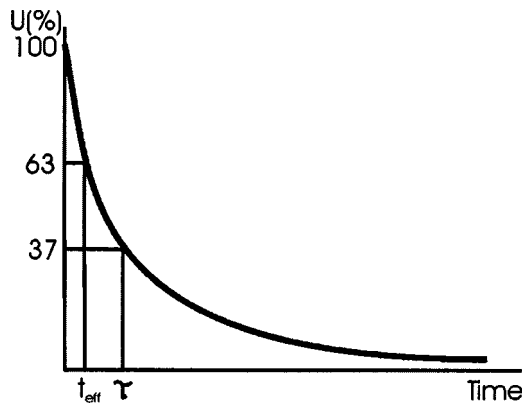


FIG. 1. Effective stress time t_{eff} and intrinsic time constant τ when discharging a capacitor. U is the electric stress over the capacitor.

where $\mu[\text{m}^2/\text{Vs}]$ is the mobility of the ion. The time t_{tr} it takes an ion to travel the distance d between the electrodes is given by

$$t_{\text{tr}} = \frac{d}{v} = \frac{d}{\mu E}. \quad (3)$$

The effect of the injected charge will be significant if $\tau > t_{\text{tr}}$.

For millisecond time scales, the maximum E -field is not only determined by the normal breakdown level of the dielectric and the area of the electrodes, but also by the *effective stress time*,³ which is defined as the time the cell experiences more than 63% of the initial stress (see Fig. 1). Furthermore, the breakdown is a statistical process and, as such, depends on the physical area of the electrodes.

A voltage-pulse technique has previously been used to probe the electric breakdown field close to the electrodes in water mixtures.^{18–22} A voltage pulse $U(t) = U_{\text{max}}(1 - \cos \omega t)$ was applied between two electrodes, and U_{max} was slowly increased in steps until a breakdown occurred. This test was performed for pure water and for water/ethylene-glycol mixtures, with an effective stress time of about 100 μs . Based on those results, an empirical formula for dielectric breakdown in 1% of the tests was derived:³

$$E_{1\%} = (17.2 \pm 5.1) A^{-(0.09 \pm 0.03)} [\text{MV/m}], \quad (4)$$

For cold pure water, 1°C , $\rho = 8 \text{ G}\Omega \text{ m}$, $\epsilon_r = 90$,

$$E_{1\%} = (36.0 \pm 4.0) A^{-(0.20 \pm 0.05)} [\text{MV/m}], \quad (5)$$

For ethylene glycol 60% water 40%, -23°C ,

$$\rho = 200 \text{ G}\Omega \text{ m}.$$

The area effect is more pronounced for ethylene glycol mixtures.

The objective of this article is to experimentally investigate the dependence of charge injection, storage time, and energy density for a water/methanol dielectric capacitor in a quest to enable the use of an inductive primary storage. Methanol is used since it is a better antifreeze than ethylene glycol,²³ has a higher dissociation constant,²⁴ and is also

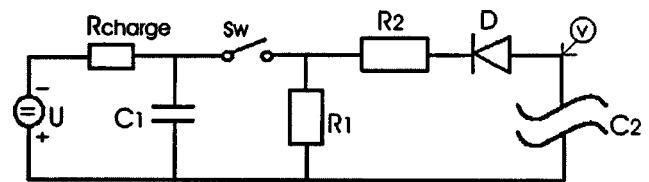


FIG. 2. The electrical circuit for charging the water capacitor and studying the self-discharge. C_1 is the primary storage and C_2 is the water capacitor. $R_{\text{charge}} = 500 \text{ M}\Omega$, $C_1 = 26.7 \text{ nF}$, S_w is a spark gap, $R_1 = 9.9 \text{ k}\Omega$, $R_2 = 792 \Omega$, D is a diode, V is a voltage probe, and $C_2 \approx 1.62 \text{ nF}$.

more electronegative. The dissociation constant is related to the concentration of ions in a solvent with respect to temperature:⁷

$$\ln K_w \sim \frac{1}{T}. \quad (6)$$

Electronegativity describes the tendency of an atom to attract bonding electrons.²³

II. EXPERIMENTAL SETUP

Two circuits were built, one for measuring τ shown in Fig. 2, and one for measuring the electric breakdown strength of the water/methanol mixture. The primary storage was charged through the R_{charge} resistor. When the spark gap S_w closes, energy from the primary storage is transferred to the water capacitor through R_2 and D . Fast recovery diodes with a recovery time t_{rr} of 50 ns were used to prevent the charge in the water capacitor from leaking back through the diodes, thereby leaving the water capacitor virtually uncharged. The remaining energy in the primary storage was discharged through R_1 to ground.

The electrical stress across the water capacitor will rapidly decrease due to the self-discharge of water and the relatively small capacitance of the capacitor. In order to maintain an electric stress high enough to enable the breakdown strength measurements of the water/methanol mixture, a new 20-nF capacitor was connected in parallel with the water capacitor. At the same time C_1 was replaced with a higher capacitance 167 nF and R_1 and R_2 were changed to 50 and 9.9 k Ω respectively.

A cylindrical water capacitor made of two concentric stainless steel tubes was used. The inner tube is 100 mm long with a radius of 18.5 mm and is rounded off on both sides with a stainless steel half-sphere of height 24 mm. The outer tube is 200 mm long with an inner radius of 25 mm. The distance between the electrodes is then 6.5 mm. The capacitance calculated using a finite element method (FEM) simulation package is then

$$C = 16.8 \epsilon_r [\text{pF}]. \quad (7)$$

The water capacitor was immersed in an 80-L tank containing the water/methanol mixture. The tank itself stood in a freezer, which could be cooled to -50°C . To deionize the liquid in the tank, it was continuously pumped through a heat exchanger into a deionization filter and back into the tank through the same heat exchanger. The heat exchanger was used in order to get a good efficiency of the deionization

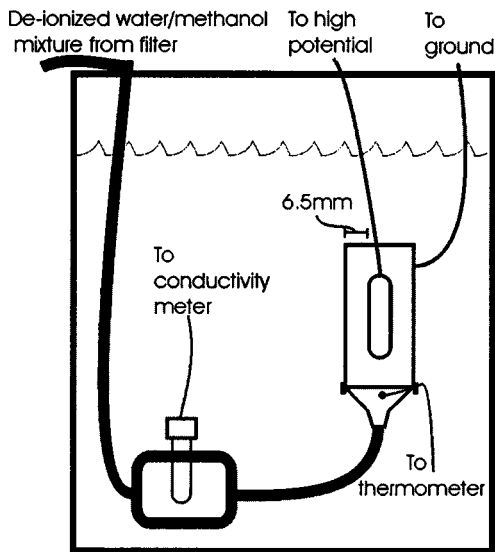


FIG. 3. The water/methanol filled tank with the water capacitor inside.

process, as that process is temperature dependent. The conductivity and temperature of the water mixture were measured just before it entered the water capacitor. Figure 3 illustrates the tank with the water capacitor in it. The water mixture flowing into the water capacitor was diffused by a conical-shaped funnel; thereby, a uniform flow between the electrodes was created.

III. LOW-VOLTAGE RESULTS

Low-voltage measurements were performed on mixtures with 51%-(Fig. 4) and 34%-(Fig. 5) by-mass methanol. Using the setup shown in Fig. 2, the water capacitor has been charged and then disconnected from the electric circuit by the diode, at which its self-discharge has been studied by measuring τ for temperatures between -20 to $+10$ °C. The influence of the charging transient on the millisecond-scale, intrinsic time constant is negligible since the charge time is about $6 \mu\text{s}$.

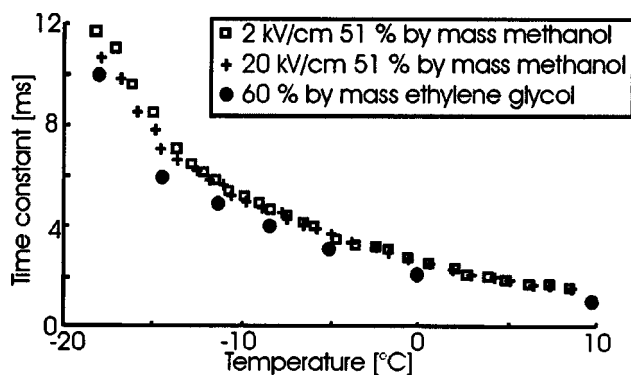


FIG. 4. The intrinsic time constant τ as a function of temperature for the 51%-by-mass methanol/water mixture. Large dots represent values attained with 60%-by-mass ethylene glycol (see Ref. 8).

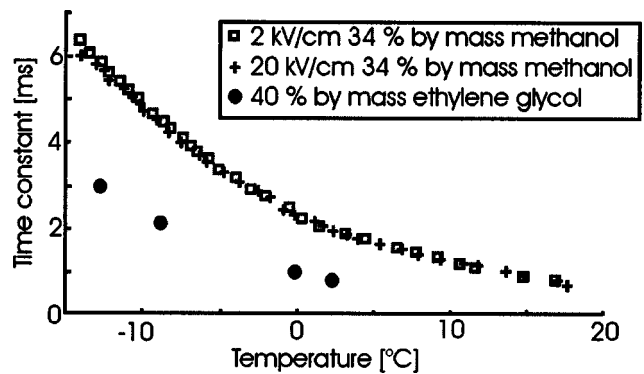


FIG. 5. The intrinsic time constant τ as a function of temperature for the 34%-by-mass methanol/water mixture. Large dots represent values attained with 40%-by-mass ethylene glycol (see Ref. 8).

IV. HIGH-VOLTAGE RESULTS

For safety reasons, due to the risk of explosion and fire, only the 34%-by-mass methanol/water mixture was used when high voltages and breakdowns were studied. The setup shown in Fig. 2 was used in the same manner as for the low-voltage measurements. Measurements were performed at seven different temperatures (-21 , -19 , -14 , -6 , 0 , $+11$, and $+18$ °C). For each temperature, starting at a low electric stress, discharge curves were recorded and τ extracted. The electric stress was increased in steps of 1.5 MV/m until 7 MV/m was reached, and then in steps of 0.5 MV/m until an electric breakdown occurred. In Fig. 6, the intrinsic time constant $\tau(E, T)$ is plotted, where the straight lines are least squares fits to the data, showing how τ for the water/methanol mixture depends on the temperature and the initial electric field E . It can be seen that lower temperature results in longer τ , as could be expected from the decrease in auto-ionization. For longer τ , the influence of charge injection becomes larger, as is reflected in the slope of the curves. Note that for lower temperatures (longer τ), the fitted lines have steeper slopes. For $+11$ and $+18$ °C, the intrinsic time constant is so short that the effect of charge injection is hardly noticeable.

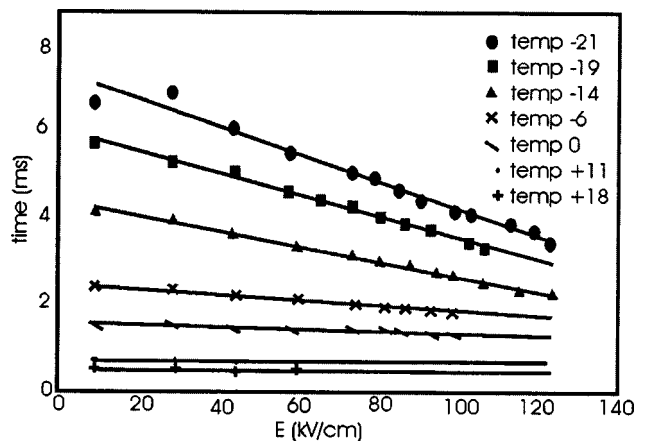


FIG. 6. The intrinsic time constant τ plotted as a function of electric field strength $\tau(E, T)$, with lines made by linear regression.

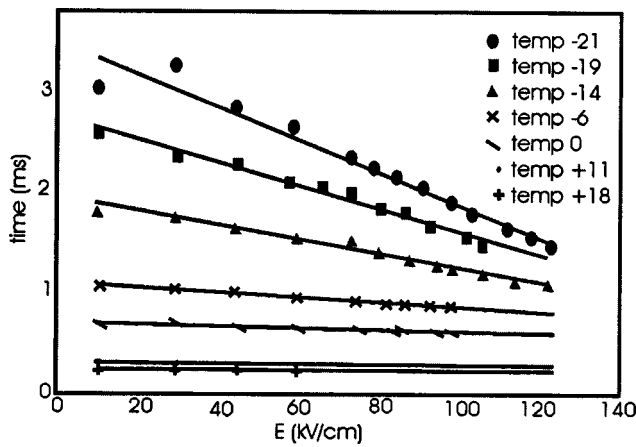


FIG. 7. The effective stress time plotted as a function of electric field strength $t_{eff}(E,T)$.

Figure 7 shows the effective stress time t_{eff} as a function of electric field E and temperature T . The stress time also shows a linear dependence between t_{eff} and the electric field. Comparing normalized values at a given temperature will show that t_{eff} has a stronger dependence on E than τ has. This is most likely caused by the higher average electric field from time zero to t_{eff} than the average electric field from time zero to τ .

Close to the electric breakdown field, steps of 0.2 MV/m were taken, and the values given in Fig. 8 represent the highest electric stress achieved without breakdown for five shots in sequence. The same measurements were made using the breakdown circuit, also with a step of 0.2 MV/m, the result plotted in Fig. 8 is again the highest electrical stress achieved without breakdown for five shots in sequence. Average time between the shots was four minutes.

The cylindrical capacitor did not have a homogeneous distribution of the electric field, instead, there was a field enhancement close to the inner electrode of about 8.6% (calculated by using a FEM simulation program). The field enhancement has been disregarded when calculating the

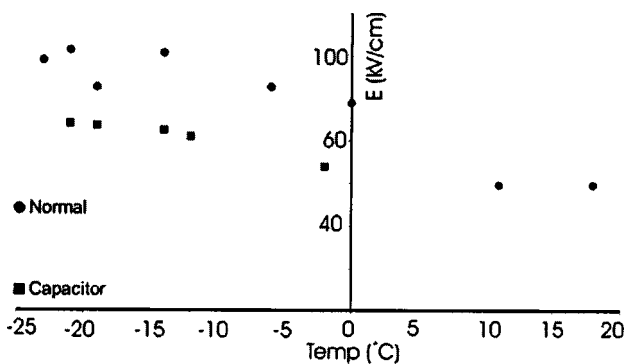


FIG. 8. Dots show the maximum stress before breakdown with just the water capacitor. Squares show the maximum stress before breakdown with a 20-nF capacitor in parallel with the water capacitor. It is evident that the water capacitor can withstand a high potential, before an electric breakdown, when the electric stress is applied for a short time. When the electric stress over the water capacitor is applied for a longer time, breakdown will occur at lower electric stresses.

TABLE I. Electrical breakdown strength for different water/ethylene glycol mixtures in a parallel-plate capacitor (see Ref. 3). E_{max} is defined as the highest electric stress without breakdown for ten tests, X is the percent (by mass) ethylene/glycol. t_{eff} is the effective stress time (the time that the electric stress is larger than 63% of the initial electric stress), temperature T , intrinsic time constant τ , relative permittivity ϵ_r , the amount of energy that can be stored W_{max} , and the action density A .

| X (%) | T (°C) | τ (ms) | t_{eff} (ms) | E_{max} (MV/m) | ϵ_s | W_{max} (kJ/m ³) | A (Js/m ³) |
|---------|----------|-------------|----------------|------------------|--------------|--------------------------------|--------------------------|
| 40 | 25 | 0.20 | 0.10 | 16 | 67 | 76 | 8 |
| 40 | -11 | 2.70 | 0.40 | 16 | 79 | 90 | 36 |
| 60 | 30 | 0.30 | 0.18 | 16 | 58 | 66 | 20 |
| 60 | -23 | 15.00 | 0.97 | 14 | 77 | 67 | 65 |

E -field; therefore, the true maximum value of the electric field is somewhat higher than the values given here.

V. DISCUSSION

The low-voltage experiments showed that τ maintained its exponential increase with decreasing temperature, as expected by Eq. (6). Intrinsic time constants of 12 ms for the 51%-by-mass methanol mixture at -18 °C and 7 ms for the 34%-by-mass methanol mixture at -15 °C were achieved. Experimental difficulties with the heat exchanger while performing low-voltage measurements excluded temperature reduction below -22 °C.

In Table I, the ability to store energy for the water/ethylene glycol mixtures, investigated in Ref. 3, is given. In Table II, the water mixture with 34%-by-mass methanol is tabulated. The tables contain three different figures of merit: E_{max} ; $W_{max} = \frac{1}{2}\epsilon_0\epsilon_r E_{max}^2$; and the action density $A = W_{max} t_{eff}$. The value of A is preferably as high as possible, as it is a measurement of the capacitor's ability to keep the maximum stored energy.⁸ Cooling enhances A and restores the dielectric constant of the mixture to near that of water.

At -11 °C, the 40% ethylene glycol/water mixture has a longer τ and a higher breakdown field than does the -13 °C methanol/water mixture. However, the effective stress time and the action density A are higher for the water/methanol mixture. At -23 °C, the effective stress time and action density are larger for the 34%-by-mass methanol mixture than for the 60%-by-mass ethylene glycol mixture. From the relationship between τ and t_{eff} , it can be seen that the effect of charge injection is much less in the water/methanol mixtures

TABLE II. Electrical breakdown strength for water/methanol mixture in a cylindrical capacitor. X is the percentage by mass of methanol and E_{max} is the highest electric field before breakdown (in the cylindrical capacitor).

| X (%) | T (°C) | τ (ms) | t_{eff} (ms) | E_{max} (MV/m) | ϵ_s | W_{max} (kJ/m ³) | A (Js/m ³) |
|---------|----------|-------------|----------------|------------------|--------------|--------------------------------|--------------------------|
| 34 | +18 | 0.42 | 0.19 | 5.9 | 61 | 9 | 2 |
| 34 | +12 | 0.61 | 0.25 | 5.9 | 63 | 10 | 3 |
| 34 | 0 | 1.26 | 0.58 | 9.8 | 67 | 28 | 17 |
| 34 | -6 | 1.8 | 0.85 | 9.7 | 69 | 29 | 24 |
| 34 | -13 | 2.23 | 1.05 | 12.1 | 71 | 46 | 48 |
| 34 | -19 | 3.25 | 1.45 | 10.5 | 74 | 36 | 52 |
| 34 | -20 | 3.37 | 1.44 | 12.2 | 75 | 49 | 71 |
| 34 | -22 | 3.71 | 1.59 | 11.8 | 76 | 47 | 74 |

than it is in the water/ethylene glycol mixtures; this is attributed to the greater electronegativity of methanol. The maximum energy density achieved was 54 kJ/m^3 or 61 J/kg . The maximum action density achieved was 74 Js/m^3 .

The breakdown strength measured with the breakdown circuit is lower than the breakdown strength recorded when measuring the time constant. Since E_{max} is expected to depend on the duration of the applied stress, this is attributed to the difference in dielectric stress times.

VI. SUMMARY

In order to enable inductive charging of a water capacitor, intrinsic time constants of a few milliseconds are needed. By using water/methanol mixtures at low temperature as the dielectric medium, the water capacitor shows intrinsic time constants well above the millisecond level, even at high electric stress (3.4 ms at 12 MV/m).

For slowly charged systems, charge injection plays a significant role for the ability to store energy. The results presented in Table II suggest that the effect of charge injection is less in water with methanol as antifreeze compared to water with ethylene glycol. However, the breakdown strength of water/methanol (12.5 MV/m) is lower than that for water/ethylene glycol, revealing that the maximum energy stored is smaller for water/methanol. However, when taking charge injection into account, water/methanol delivers more usable energy to the load; the action density A at -23°C is 74 Js/m^3 . Thus, water/methanol mixtures appear to offer a path towards the use of inductive primary storages in pulsed-power systems.

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