DC surface flashover characteristics of ZnO/Epoxy composites at room temperature and 77 K

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Abstract. Epoxy (EP) resin based nano-composites are widely used in high voltage direct current (HVDC) high temperature superconducting (HTS) power cable. In this paper, the DC surface flashover characteristics of ZnO/EP composites were studied at both room temperature and 77 K. The samples were made by dispersing ZnO nano-particles into EP resin with various weight percentages of 0%, 1%, 3%, 6% and 10%, respectively. The experiments were carried out with a cryogenic system in which DC high voltages ranging from 0 kV to 100 kV were supplied. The results showed that the surface flashover voltages increased with the increase of ZnO content at both room temperature and 77 K, and the surface flashover voltages at 77 K were higher than that at room temperature for composites with the same ZnO content.

1. Introduction

High temperature superconducting (HTS) power cable is used in high voltage direct current (HVDC) transmission. The operating temperature of the cable termination ranges from room temperature to 77 K, and the termination is exposed to high electrical field which can cause surface flashover or breakdown of the insulating structure [1, 2]. For solid insulation, the surface flashover voltage is usually much lower than the breakdown voltage [3]. Therefore, it is of great significance to study the surface flashover characteristics of insulating materials at both room temperature and 77 K.

At present, researchers have studied surface flashover characteristics of various materials used in the insulating structure of the HVDC HTS cable. For example, Kim S H et al [4] have found that the
surface flashover voltages of GFRP, Bakelite and Teflon were nearly equal at 77 K. In addition to these materials, EP resins doped with various inorganic fillers were widely used. Chen Y et al [5] have studied surface flashover characteristics of EP resins containing different kind of micro-inorganic oxide particles such as Al₂O₃, BaTiO₃ and TiO₂ under nanosecond pulse. The results showed that the surface flashover voltages of the composites were lower than that of the pure EP. Li T et al [6] have found that the DC surface flashover voltage of the TiO₂/EP nano-composites was higher than that of pure EP. The difference was due to the fact that the surface flashover voltages were related to the sizes of the particles. Moreover, fillers with non-linear conductivity such as SiC were used to reduce the surface charge accumulation thus increase the surface flashover voltage. 

ZnO is a new type of filler. Researches have found that the inclusion of ZnO nano-particles in EP resin could produce non-linear conductivity behavior [7]. Zhang Z et al [8] have shown that the DC surface flashover voltage of the polyimide doped with 3 wt% nano-ZnO was higher than that of pure polyimide. For ZnO/EP nano-composites, surface flashover characteristics at cryogenic temperatures were rarely studied. Therefore, in this paper, the DC surface flashover characteristics of ZnO/EP nano-composites at 77 K were studied and compared with those at room temperature. The samples were made by dispersing ZnO nano-particles into EP resin with weight (wt) percentages of 0%, 1%, 3%, 6% and 10%, respectively. The experiments were carried out under a cryogenic system in which DC high voltages ranging from 0kV to 100kV were supplied.

2. Experiment

2.1 Surface modification of nano-ZnO
ZnO nano-particles (4g) and the ethanol/deionized water (50ml/100ml) solution were mixed by ultrasonic for 30 minutes (mixture I). KH560 silane coupling agent (5 wt% of ZnO), the main function of which was to enhance the adhesion between EP and ZnO particles, was dripped into the ethanol/deionized water (50ml/50ml) solution and the solution was then heated to 80°C (solution I) by a magnetic stirring device. After that, mixture I was slowly dripped into solution I and reacted at 80°C for 2 hours. Finally, ZnO nano-particles were filtered, dried and ground [9].

2.2 Preparation of the nano-composites
The modified nano-ZnO were dispersed into EP (bisphenol A, 128, South Asia epoxy Co., Ltd.) with weight percentages of 0%, 1%, 3%, 6% and 10% respectively and the mixture were mixed and stirred for 5 min at 800 rpm, 15 min at 1000 rpm by a planetary gravity mixer. Then the mixture was dispersed by ultrasonic for 30 minutes, and then curing agent (D230) was added. A rotary vacuum pump was used to degas the mixture. Finally, the mixture was poured into the mould and cured at 80°C for 3 hours. The cured samples were thin slices with the diameter of 55mm and the thickness of 1.5mm.

2.3 Test of the surface flashover voltage
The experimental setup consisted mainly of a cooling system and a DC high voltage power system. The cooling system was sealed in a cryostat cooled by a GM cryocooler (KDE 415, CSIC PengLi Cryogenic Technology Co., Ltd), including the external chamber, two radiation shields connected with
the 1st and 2nd stages, respectively. The electrode system was encapsulated in the 2nd radiation shield chamber, as shown in figure 1. High voltage was supplied by a DC high voltage power supply (DW-P104-2AC2). The surface flashover voltage was measured by an oscilloscope, as shown in figure 2. The experiment was carried out under $10^{-4}$ Pa. Each sample was cleaned in ethanol, deionized water respectively with ultrasonic before test.

![Figure 1](image1.png)

**Figure 1.** The cooling system (a) and the electrode system (b).

![Figure 2](image2.png)

**Figure 2.** The schematic diagram of the DC high voltage power system.

3. **Results and discussion**

3.1 **Results**

The test results of each sample were described by Weibull distribution. The cumulative density function are shown in equation (3.1):

$$F(U, \alpha, \beta) = 1 - \exp \left[ -\left( \frac{U}{\alpha} \right)^{\beta} \right]$$  \hspace{1cm} (3.1)

The equation (3.1) can be written in another form, i.e

$$\beta (\ln U - \ln \alpha) = \ln [- \ln (1 - F)]$$  \hspace{1cm} (3.2)

Where the scale parameter $\alpha$ represents the voltage for which the failure probability is 0.632 (that is
(1-1/e), where e is the exponential constant, when $F=0.632$, $U=a$. It is analogous to the mean of the Normal distribution [10]. Place the n flashover voltages in order from the smallest to the largest and assign them a rank from $i = 1$ to $i = n$, then $F$ can be calculated by equation (3.3),

$$F = \frac{i - 0.44}{n + 0.25}$$

(3.3)

In order to get the Weibull distribution, Let

$$X_i = \ln U$$  
(3.4)

$$Y_i = \ln [-\ln (1 - F)]$$  
(3.5)

$X_i$, $Y_i$ were plotted in figure 3 and figure 4, respectively. In both figures, the left part (a) was the diagram of the Weibull distribution while the right part (b) was the enlarged diagram of the rectangular mark in the left diagram.

**Figure 3.** The surface flashover test results at room temperature.

**Figure 4.** The surface flashover test results at 77 K.
The results obtained at room temperature were shown in figure 3. Compared with the pure EP, the surface flashover voltage of the sample containing 1 wt% ZnO increased obviously. When 3 wt%, 6 wt% and 10 wt% ZnO were added to EP, the surface flashover voltages had little difference, but were higher than that of the sample containing 1 wt% ZnO. The measurement uncertainties of $X_i$ of each sample were 0.28, 0.12, 0.25, 0.23 and 0.24 respectively.

The results at 77K were shown in figure 4. The surface flashover voltages of each sample manifested little difference. To be specific, for the samples containing 0 wt%, 1 wt%, 3 wt% and 10 wt% ZnO, the surface flashover voltages increased with the increase of the content of ZnO. The flashover voltage of the sample containing 6 wt% ZnO was slightly lower than that of samples containing 3 wt% ZnO. The uncertainties of $X_i$ of each sample were 0.12, 0.13, 0.15, 0.12 and 0.16 respectively.

The surface flashover voltages for which the failure probability were 0.632 were calculated and plotted in figure 5. It showed that the surface flashover voltages at 77 K were higher than that at room temperature for samples with the same weight percentages of ZnO.

![Figure 5](image.png)

**Figure 5.** The voltages for which the failure probability were 0.632.

3.2 Discussion

The mechanism of the surface flashover phenomenon in vacuum can be explained by the SEEA (Secondary Electron Emission Avalanche) model and the ETPR (Electron Triggered Polarization Relaxation) model. According to the SEEA model, the initial electrons, emitted from the triple-junction of the material-vacuum-cathode due to the distortion of the electrical field, will hit the material and produce the secondary electrons. The initial electrons and the secondary electrons will continuously hit the material and lead to electron avalanche. Meanwhile, the adsorbed gas on the surface of the material will be removed. Oxygen released will capture the electrons and then carry negative charges, moving with the electrons towards the anode. When the electrons form a channel connecting the cathode and anode, the surface flashover occurs. According to the ETPR model proposed by Blaise G [11], trapping centers and space charges can be found inside the insulating material. External turbulence can lead to the depolarization of the material. The stored electrostatic
energy released by charge relaxation can contribute to the surface flashover. To study the influence of space charges and trap levels on the surface flashover voltage, TSDC (Thermally Stimulated Direct Current) were measured. Samples were polarized by electrical field of 5 kV/mm at 300 K for 20 min, and then were cooled to 250 K rapidly. Depolarization currents were measured while the samples were heated with the rate of 5 K/min. The results were shown in figure 6. The trapped charges Q and the activation energy E were calculated according to the method proposed by Singh S D et al [12]. The results were shown in table 1.

![Figure 6. TSDC of each sample (a~e).](image_url)
As shown in Table 1, the activation energy of each sample increased with the increase of the content of ZnO, meaning that the trap levels were deeper. The charge carriers trapped in the deep traps were more difficult to escape than those trapped in the shallow traps, thus the development of the electrons avalanche of the samples containing deep traps was not as rapid as that of the samples containing shallow traps. Moreover, samples containing more space charges would release more charges and energy in the process of depolarization, contributing to the development of the surface flashover.

At room temperature, it was assumed that the pure EP contained more space charges and the trap level was shallow, hence the surface flashover voltage was the smallest of all the samples. For the samples containing 1 wt%, 3 wt% and 6 wt% ZnO, especially for the sample containing 1 wt% ZnO, due to the fact that the trap levels were deeper and the amount of the space charges decreased obviously, the surface flashover voltages increased obviously. For sample containing 10 wt% ZnO, although the trap level of it was deeper than that of the other samples, the space charges of it were much more than that of the other samples (except the pure EP), either. Hence the surface flashover voltage of it was close to that of the samples containing 3 wt% and 6 wt% ZnO.

At 77 K, it was considered that due to the decrease of the amount of the initial electrons emitted from the triple-junction, the amount of the secondary electrons decreased. Although the trap levels of ZnO/EP composites were deeper, the effect of the levels of traps was not as significant as that of the temperature. Therefore, with the increase of the content of ZnO, the surface flashover voltages tended to increase, but the increase was slight.

Moreover, according to Blaise G [11], the depolarization process, during which much energy would be released, can contribute to the surface flashover. The depolarization process can be triggered if trapping centers were hit by electrons. It was assumed that the electrons with a lower density were less likely to trigger the depolarization process compared to those with a higher density. Therefore, the depolarization process might initiate more easily at room temperature than at 77 K for samples containing the same weight percentage of ZnO.

4. Conclusion

Compared with pure EP, composites that doped with ZnO nanoparticles manifested higher surface flashover voltages at both room temperature and 77 K. Moreover, the increase of the surface flashover voltages was more observably at room temperature. The results indicated that ZnO nano-particles introduced more deep traps thus increased the surface flashover voltage. Meanwhile, for the composites with the same ZnO content, the surface flashover voltages at 77 K were higher than that at room temperature. It was due to the fact that with the decrease of the temperature, the the amount of

| Sample | Q /nC | E_i /eV | E_II /eV |
|--------|------|--------|---------|
| Pure EP | 13.35 | —      | 0.28    |
| 1%ZnO | 3.51 | —      | 0.56    |
| 3%ZnO | 0.22 | —      | 0.69    |
| 6%ZnO | 3.48 | 0.22   | 0.89    |
| 10%ZnO | 10.22 | 0.65   | 0.89    |
the secondary electrons decreased, hence the surface flashover voltages increased.

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