EFFECT OF AGING BY-PRODUCTS AT NANOPARTICLE-OIL INTERFACE ON CHARGE TRANSPORT IN AGED TRANSFORMER OIL-BASED NANOFLUID

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ABSTRACT
Transformer oil-based nanofluids (NFs) with TiO2 semiconductive nanoparticles (SNFs) exhibit substantially higher AC breakdown voltage than that of pure transformer oils at variable aging time from 6 days to 36 days. Charge accumulation and decay characteristics of pure oils and SNFs were measured by the pulse electroacoustic technique (PEA). It reveals that SNFs have more uniform internal electric fields and higher charge decay rate compared to pure oils under long time aging condition. It is confirmed by the test results of electrophoresis and thermally stimulated current (TSC) that the nanoparticles adsorb aging by-products molecules at the nanoparticle-oil interface, giving rise to the higher shallow trap density and resulting in better charge transport in SNFs.

KEYWORDS: *nanofluid; nanoparticle-oil interface; charge transport; shallow trap; aging*

I. INTRODUCTION AND BACKGROUND

Transformer oil is one of the key insulation liquids in worldwide high-voltage transformers and its high dielectric strength provides insulation support for achieving normal operation [1]. It has been found that once the transformer oil has been aged, the chance for the organic polar molecules and organic acid to form clusters is increased[2], leading to more 'weak links' and space charge accumulation under the electrical stress which distorts the internal local electric field and deteriorate the insulation property [3,4]. Much effort has been done to measure and understand the influences of aging on breakdown performance of transformer oil as they are not only scientifically challenging but also practically important [5-7]. However, how to have a uniform internal electric field and improve the breakdown voltage to recycle the used transformer oil is still a big challenge.

Our recent work has found that the addition of semiconductive nanoparticle is helpful to the transport of charge carriers in the oil media [8]. In this paper, we try to dissipate the accumulated space charge and have higher insulating strength, uniform electric field in the transformer oil by adding TiO_2 semiconductive nanoparticles into aged transformer oil. The associated modification mechanism is proposed.

II. PREPARATION AND BREAKDOWN STRENGTHS OF NANOFLUIDS

Pure transformer oil was fully aged at an elevated temperature of 130 °C according to the IEC 61125A standard. The acidity was measured every 6 days by a Metrohm 877 Titrino Plus. It is found that its acidity value has exceed the limit value for operating transformer oil (0.1 mgKOH/g) after 36 days.The modified aged oil was produced by adding a certain amount of TiO_2 nanoparticle into it, obtaining the nanofluid with long time high colloidal stability. The method has been described in our previous study [9].

Water content of all samples was 10 ppm measured by a Metrohm 831 KF Coulometer. AC breakdown voltages of SNFs and pure oil samples were measured according to the ASTM D1816 standard. Table 1 summarizes the breakdown voltage of pure oil and nanofluid. It is clearly seen from Table 1 that breakdown voltages of oil decrease significantly with aging time increase. However, the breakdown voltages of nanofluid almost keep constant, indicating that the ac insulation level of aged oil has been recovered by nano-modification.

Table I. AC breakdown voltage of oil and nanofluid

Aged days	oil	nanofluid
0	67.8	80.9
6	60.8	62.9
12	59.4	64.5
18	56.2	64.9
24	40.4	65.6
30	39.4	64.5
36	28.5	63.1

III. RESULTS AND DISCUSSIONS

3.1. Charge transport characteristics

To understand breakdown phenomenon in the insulating materials, the distribution of space charge and the internal electric field has been considered as a key component [10-12], which can be assessed by the PEA [13]. The setup and procedures of the PEA experiment are given before [9], and our samples have a thickness of 100 μm. During the experiment, a negative DC high voltage was applied to the sample and the distribution of charge in the sample was recorded every 10 minutes. After 30 minutes, DC high voltage was powered off and then the change of space charge distribution is measured at time intervals of 8 s. The electric field distributions in the samples are calculated by integrating the charge density:

$$E(x) = \int_0^x \frac{\rho(x)}{\varepsilon_0 \varepsilon_r} dx, 0 \le x \le d \qquad (1)$$

Where, $\rho(x)$ is the charge density,

d is the thickness of sample,

the dielectric permittivity ε_r of oil is 2.2 and that of nanofluid is 3.8.

Fig. 1 shows how the local electric field distributions change with time for the un-aged pure oil and nanofluid, stressed at 16 kV/mm DC. The positions of electrodes are confirmed and marked with black solid lines in the figures. The internal field in oil is increasing with time, approximately 121% of the applied field, which enhances the chance to initiate breakdown at lower voltage. However, the maximum electric field in SNFs is reasonably reducing with time. The field in the SNFs appears to be closer to the average field throughout the material with time increase, i.e. it is never more than approximately 113 % of the applied field.

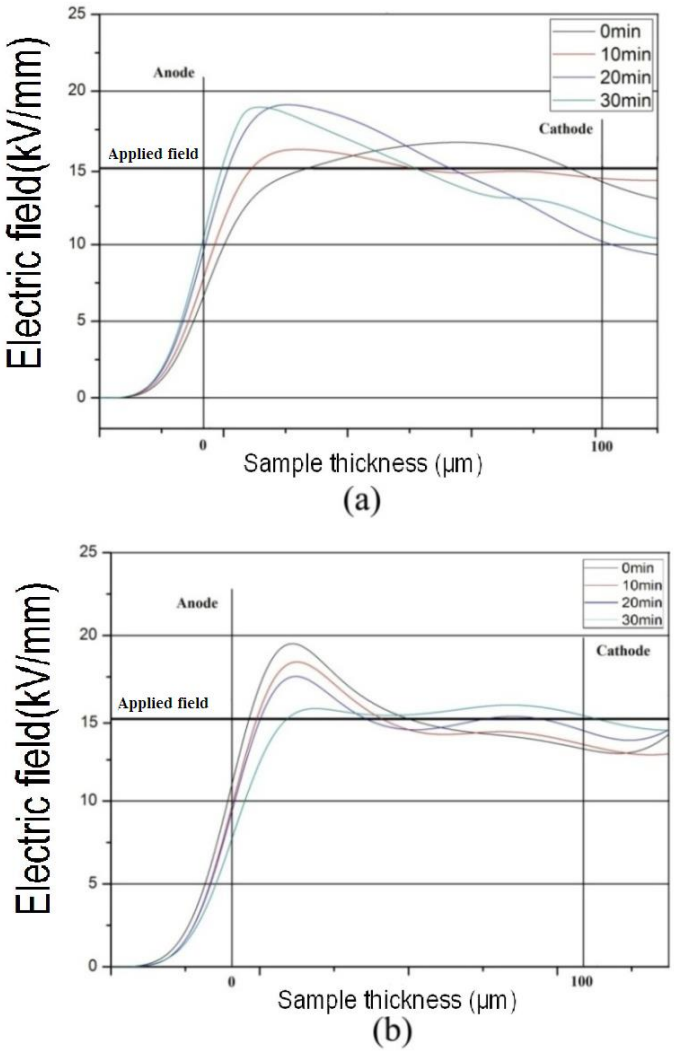

Figure. 1. Development of the electric field in un-aged pure oil (a) nanofluid (b).

When the aging period is longer than 18 days in the samples, the PEA curves show more substantial differences between the oil and nanofluids, as illustrated in Fig. 2, representing electric field distribution changes with time for samples of aged 36 days. The maximum internal fields in oil are increasing with time from 17.6kV/mm to 23kV/mm, approximately 148% of the applied field. As shown in [14], the presence of polar molecules gives rise to facile charge accumulation and electric field distortion. However, the maximum electric field in SNFs is reasonably reducing with time from 25.5kV/mm to 18kV/mm. The field in the SNFs appears to be 'evening out' after 20 minutes, i.e. it is never more than approximately 116 % of the applied field. It is considered that nanoparticles impair

the effect of aging on accumulation of electric field in oil.

It is clearly seen from Fig. 1 and Fig. 2 that the maximum electric fields in oil and SNFs both become bigger along with the degree of deterioration increase. However, the maximum electric fields in SNFs are 93% and 78% of those in un-aged and aged oil respectively. It is interesting to notice that the discrepancy of electric field between SNFs and pure oil become more and more obvious with the degree of deterioration increases, indicating more improvement of electrical strength in SNFs.

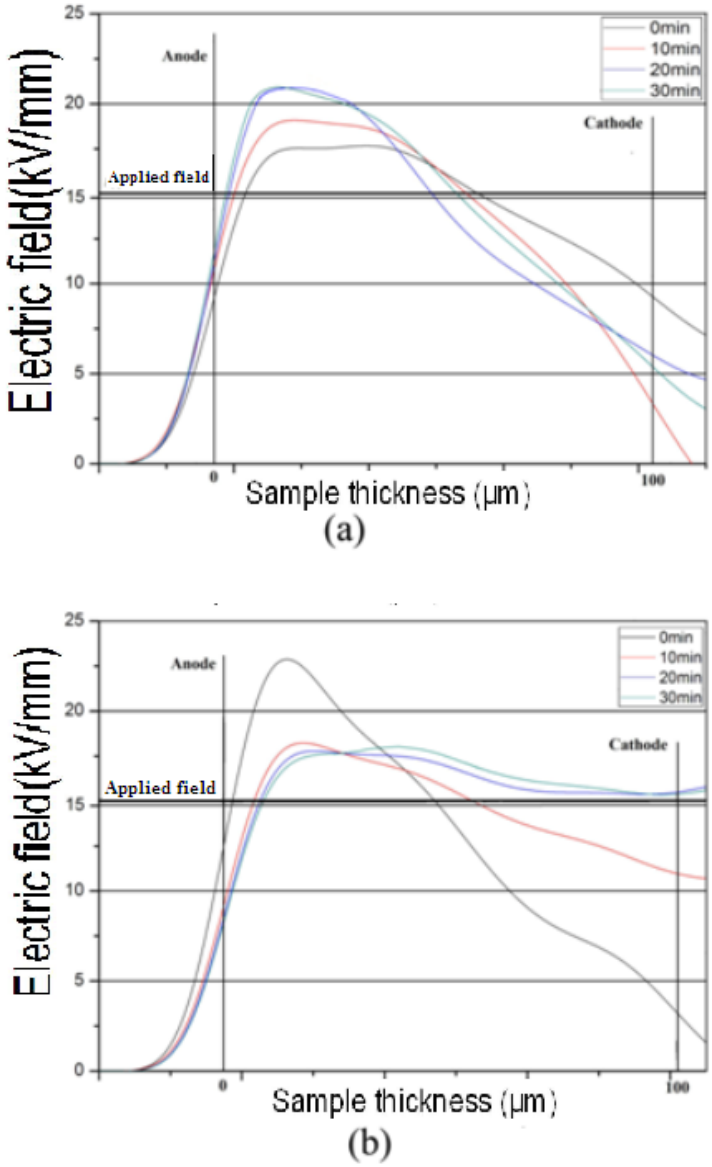

Figure.2 Development of the electric field in aged pure oil (a) and nanofluid (b).

Space charge studies show that nanofluid exhibits lower and redistributed electric field attributed to a fast charge decay rate [8]. The charge distributions in the un-aged oil and SNFs change with time after the removal of the applied voltage, shown in Fig. 3. The anode peak is sharp and evident. In contrast, the cathode peak is wide and flat because of attenuation and scattering of acoustic wave caused by fluid material. For this reason, the analysis of the space charge decay is concentrated on the space charge close to the anode [15]. It is noted in Fig. 3 that the proportions of charge decay in oil and SNFs are 80.7% and 92.8% at t=16S. The charge decay rate for SNFs is 1.30 and 1.16 times of that for pure oil in the first 8 S and 16 S respectively after the voltage is removed. This rapid charge decay

rate is mainly associated with TiO_2 nanoparticles in SNFs and effectively prevents the charge accumulation and the distortion of electric field in the oil, which is also observed in solid dielectric nanocomposites modified by TiO_2 nanoparticles [10,16].

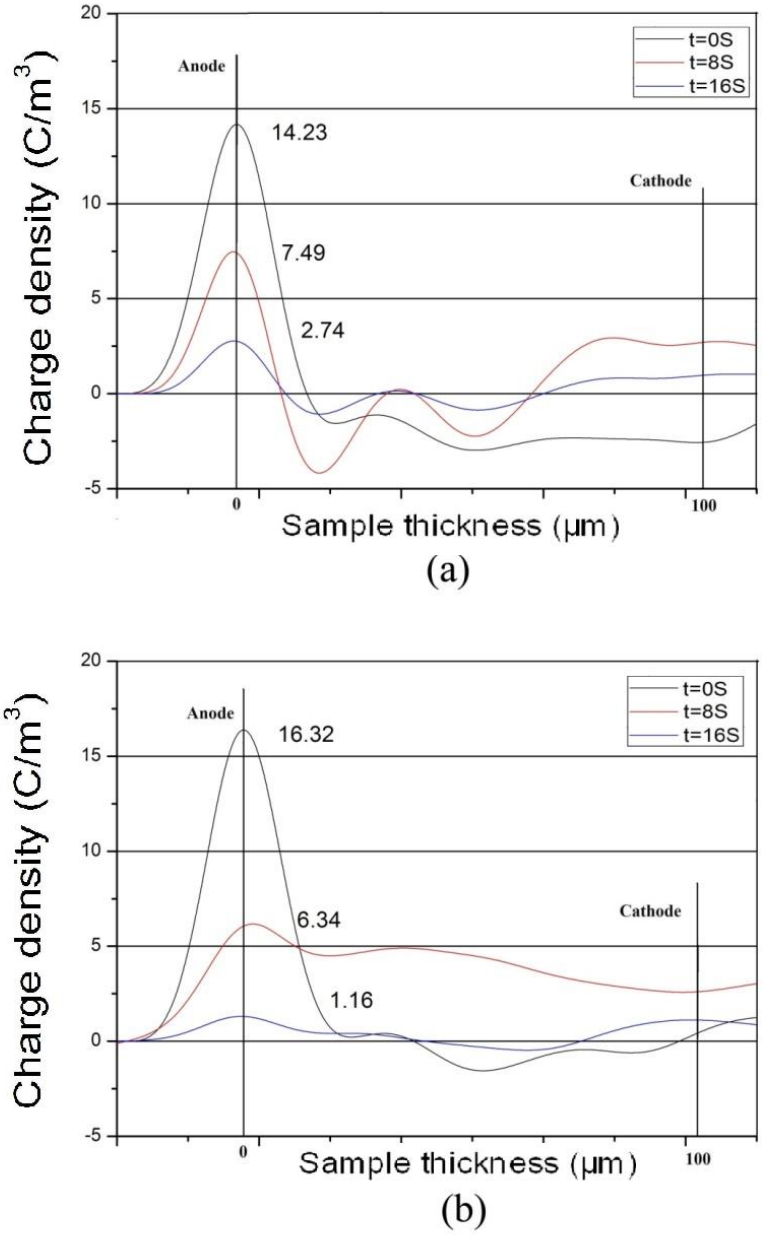

Figure. 3. Charge decay in new oil (a) and nanofluids (b) after the voltage removal.

The charge distribution in the aged samples changes with time after the removal of the applied voltage, shown in Fig. 4. It is noted in Fig. 4 that the charge decay proportions in oil and SNFs are 62.4% and 75.4% at t=16S. The charge decay rate for SNFs is 1.55 and 1.21 times of that for pure oil in the first 8 S and 16 S respectively after the voltage is removed.

Along with the degree of deterioration increase, it is clearly seen from Fig. 3 and Fig. 4 that the proportions of charge decay in oil and SNFs both become smaller. However, the ratio of charge decay in SNFs to that in pure oil is bigger in aged samples. This bigger discrepancy of charge transport give rise to more improvement of electric field in SNFs.

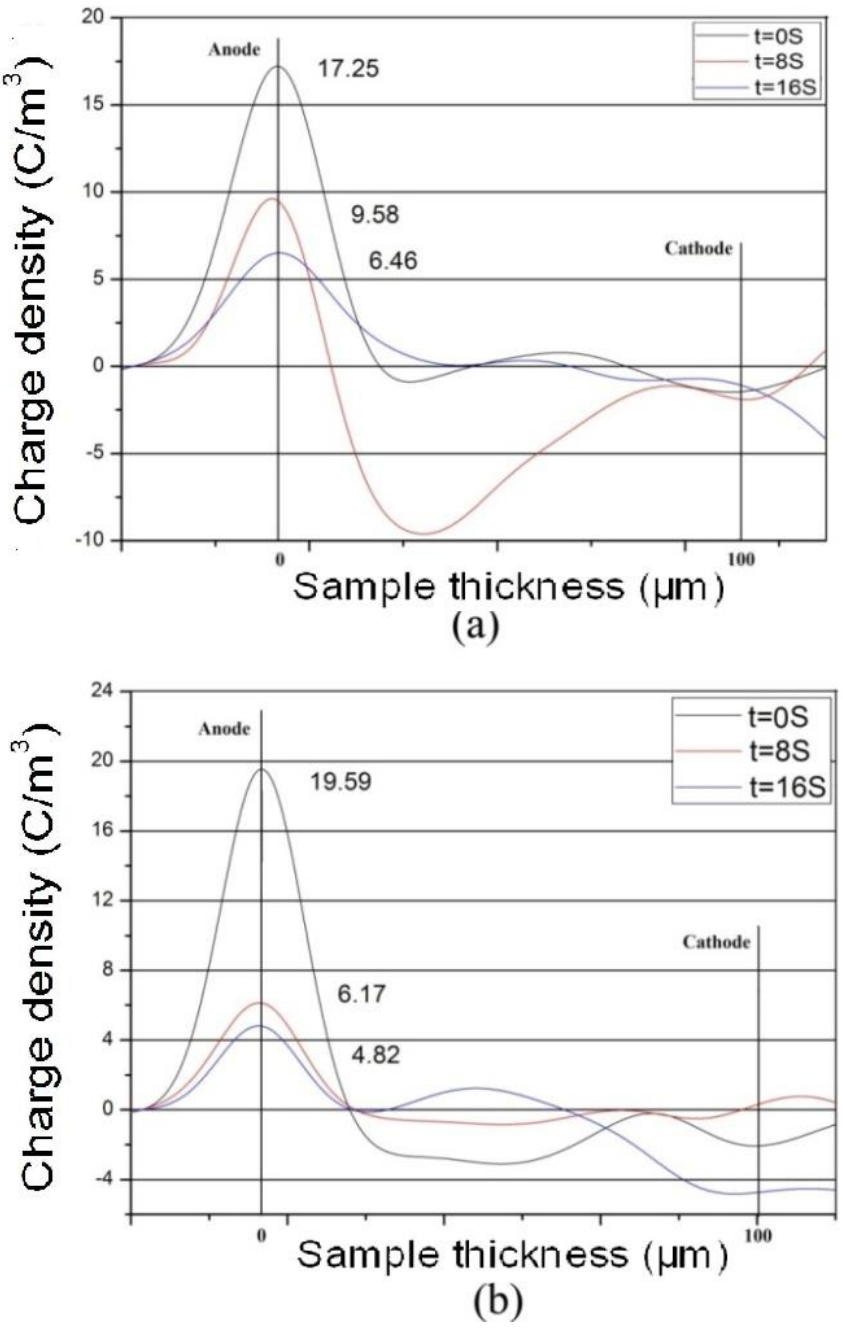

Figure. 4. Charge decay in aged oil (a) and nanofluids (b) after the voltage removal.

Due to the similar feature of charge and electric field in the same kind of sample when aging time is longer than 6 days, other PEA results are not listed in the paper.

3.2. Trap distribution Characteristics

The fast charge decay seen both in uniform and divergent fields could be linked to relatively shallow traps existing in a nanocomposite compared to a base matrix [8,10]. In order to investigate the relationship between charge transport and the trap characteristics, TSC measurements were performed using samples of thickness 100 μm. It is believed that TSC measurements can be used to investigate the nature and origin of charge carrier traps in dielectrics, including the change of the number and energy of the trap sites [17,18]. The setup and procedures of the TSC experiment are given before[9]. In order to ensure the accuracy of the test, the TSC curves shown in Fig. 5 and Fig. 6 are the average

of three test data, whose peak position is found to be reproducible within ±2ºC.

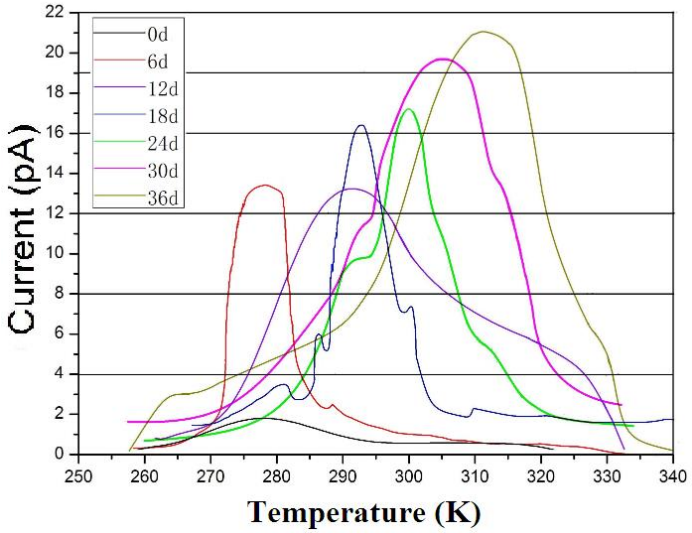

Figure. 5. TSC test results of aged oil stressed at 4 kV/mm.

It is seen on the TSC curves in Fig. 5 that a deeper trap center with larger peak value is formed with aging time increase in oils, which is also observed in solid dielectric aging tests [19]. Compared with oil, the trap center is shallower and the peak value is larger in SNFs at any aging time in Fig. 6. It is interesting to note that the shallow trap center and peak value is reasonably constant in SNFs and the discrepancy between oil and SNFs become more obvious with aging time increase. Since the peak value of the TSC curve is related to maximum trap density in a dielectric [20], SNFs have a higher shallow trap density than that of oil. Therefore, SNFs yield higher charge decay rate and less charge accumulation, preventing the distortion of electric field caused by the presence of a large amount of shallow traps.

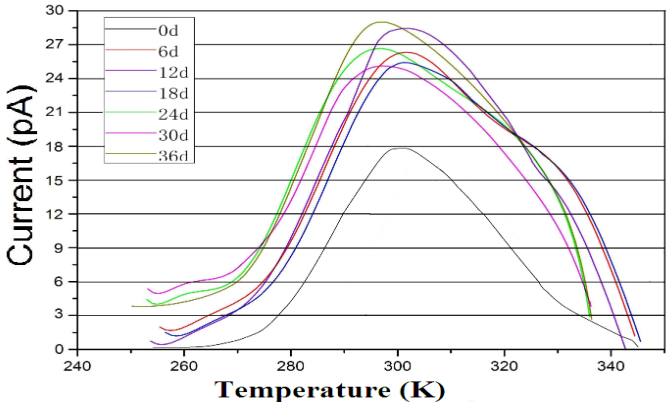

Figure. 6. TSC test results of nano modified aged transformer oil stressed at 4 kV/mm.

3.3. Electrophoresis measurements

The trap density and the depth of trap sites in dielectric may be altered by the change of local structure [15]. In the case of nanoparticles, the surface area in contact with the oil is dramatically increased and creates large interaction zones formed at the internal interfaces. In the interaction zone, the TiO_2 nanoparticle has a surface charge (due to the differences in Fermi level between the nanoparticles and oil), that creates a Stern layer surrounded by a diffuse Gouy–Chapman layer. This

Gouy–Chapman–Stern layer induces altered local structure in the vicinity of the nanoparticles, which may give rise to altered affinity for polar molecules and the corresponding trap characteristic [21-23]. Hence, electrophoresis measurements were carried out to investigate the Zeta potential which can represent the change of structure at a solid-liquid interface and indicates the short-range interaction (such as specific adsorption) between Gouy–Chapman–Stern layer and the surrounding substance, using a Malvern ZS90 electrophoresis apparatus. Table 2 summarizes the Zeta potential of SNFs with variable aging time. It is clearly seen that the Zeta potential appeared to be constant except the un-aged sample. It is in agreement with the observation in Fig. 6 that the electron trap properties of variable aged samples are similar, which differ from the un-aged one. Hence, it is believed that TiO_2 nanoparticle change the interaction between aging by-product and oil molecules by bind the aging by-products molecules to the Gouy–Chapman–Stern layer and then modify the trap characteristics.

Table 2. Zeta potential of nanofluid with variable aged days

Aged days	Zeta potential (mV)
0	-14.1
6	-2.10
12	-2.34
18	-2.61
24	-3.56
30	-3.50
36	-3.94

IV. MODIFICATION MECHANISMS

The Gouy–Chapman–Stern layer is the pathway whereby charge would be transferred between nanoparticles and oil, which plays a great role in improving the dielectric strength of nanofluid. Based on the results of Zeta potential, TSC and PEA measurements, a fraction of aging by-product molecules are bound to the nanoparticle-oil interface and form an ordered layer [24,25], which will enhance the lateral conductive path along the interface, leading to the creation of a high local conductivity. The change of interfaces could be a major factor for higher shallow trap density in SNFs with aging time increase. It could be believed that shallow traps are associated with a charge hopping transport process in the sample and the charge carriers created at high field in the SNFs can be captured by the shallow traps and released rapidly from these shallow traps. Rapid transfer of charge carriers in the shallower traps results in their larger mobility in SNFs than oil in high field, which significantly mitigate the accumulation of space charge and electric field distortion caused by aging periods.

V. CONCLUSIONS

In summary, the test results indicate that both charge dissipation velocity and shallow trap density in SNFs are obviously increased compared to that in oil with aging time increase. It is proposed that the strong affinity of a Gouy–Chapman–Stern layer for aging by-product molecules give rise to the

change of nanoparticle-oil interface structure and the corresponding higher shallow trap density, which results in facile charge movement by the trapping and de-trapping process, offering the more uniform internal electric field and high dielectric strength of nanofluid.

In the future, transformer oil and the associated nanofluid will be aged at an elevated temperature of 90 °C for longer time in my laboratory, which is more similar with the actual operating condition. The effect of nanoparticle will be discussed for promoting the application of nanofluid.

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BIOGRAPHY

Du Yuefan was born in Tianjin, China, in 1986. He received the Bachelor and Ph.D in Electric and Electronic Engineering degree from North China Electric Power University, Beijing, in 2008 and 2013 respectively. His research interests include condition monitoring and dielectric theory.