The effect of nanoparticle surfactant polarization on trapping depth of vegetable insulating oil-based nanofluids

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ABSTRACT

Nanoparticles can generate charge carrier trapping and reduce the velocity of streamer development in insulating oils ultimately leading to an enhancement of the breakdown voltage of insulating oils. Vegetable insulating oil-based nanofluids with three sizes of monodispersed Fe$_3$O$_4$ nanoparticles were prepared and their trapping depths were measured by thermally stimulated method (TSC). It is found that the nanoparticle surfactant polarization can significantly influence the trapping depth of vegetable insulating oil-based nanofluids. A nanoparticle polarization model considering surfactant polarization was proposed to calculate the trapping depth of the nanofluids at different nanoparticle sizes and surfactant thicknesses. The results show the calculated values of the model are in a fairly good agreement with the experimental values.

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1. Introduction

Vegetable insulating oils have been used as substitutes for mineral insulating oils, which are the most widely used dielectric liquids in oil-filled transformers. Recent research has shown that the thermal conductivity and breakdown voltage of insulating oils can be enhanced remarkably by adding well-dispersed nanoparticles into the oils [1–7]. Magnetite nanoparticles from ferrofluids were used to prepare insulating oil-based nanofluids—both AC and DC breakdown voltages were increased at the proper composition [4,6]. The TiO$_2$ semiconductive nanoparticles also improved the dielectric breakdown performances of mineral and vegetable insulating oils [3,5,10].

Electric charge carrier transportation is influenced through trapping and de-trapping processes of charge carriers in insulation materials. Traps in an insulation material can be formed by chemical defects, such as carbonyl groups (C=O) in vegetable insulating oils [8]. They can also be induced by nanoparticles in high electrical field to create trapping sites for electric charge carriers, because the dielectric constant of the nanoparticles differs from that of the continuous medium [9]. The trapped charge carriers generate a distribution of electric potential surrounding a trap and the trapping depth is the maximum potential. Takada et al. proposed

a mathematical model to calculate the trapping depth of nanoparticles in low density polyethylene and depicted that the trapping depth depends on the size, relative dielectric constant, and shape of the nanoparticles [9]. Several studies [3,5,10] have described a physical model revealing that nanoparticles increase the trap density and reduce the velocity of streamer propagation in mineral and vegetable oil-based nanofluids. However, these publications ignored the influences of nanoparticle surfactants on the dielectric properties of insulation nanomaterial. Nanoparticles are usually non-lipophilic, and nanoparticle surface modification is an essential approach via coating surfactant on the nanoparticles to achieve long-term dispersion stability of the oil-based nanofluids [11–13]. For instance, the high temperature decomposition is a very effective method of surface modification for magnetite nanoparticles to obtain stable oil-based magnetite nanofluids. Because the physical and chemical properties of the surfactant are very different from those of the nanoparticle, the surfactant may critically influence the trapping characteristics of the nanofluids in the electric field.

This letter focuses on the influence of surfactant polarization on the trapping characteristics of a vegetable oil-based nanofluid modified with Fe$_3$O$_4$ nanoparticles. Three sizes of Fe$_3$O$_4$ nanoparticles with different thickness surfactant were prepared to fabricate vegetable oil-based nanofluids. Thermally Stimulated Current (TSC) experiments investigated the effect of surfactant thickness on the charge carrier trapping characteristics of the vegetable oil-based nanofluids. A model considering surfactant polarization was

proposed to calculate the trapping depth of the surface-modified nanoparticle.

2. Experimental

Nanofluids preparation: The Fe_3O_4 nanoparticles were obtained by the approach of high temperature decomposition [14], which produced the nanoparticles with increasing size as its reaction time increased. The insulating vegetable oil-based nanofluids were obtained in the following procedures. First, 6.48 g of iron (III) chloride hexahydrate was dissolved in the mixture of 48 mL ethanol and 84 mL N-hexane, and the obtained solution was slowly added with 21.9 g sodium-oleate-vigorous through magnetic string at 60 °C for 12 h; the solution was additionally washed three times by using deionized water at 60 °C in a separatory funnel and subsequently dried in vacuum at 80 °C for 24 h to obtain oleate precursors. Secondly, 2.1 g iron oleate precursor and 0.64 mL oleic acid were mixed in 10 mL octadecene followed by transferring the mixture into a three-neck-round-bottom flask and drying it at 120 °C for 30 min under nitrogen protection to remove water and oxygen; the mixture was then heated to 320 °C for 24 h, 48 h, and 72 h to realize Fe_3O_4 nanoparticles in various sizes; after cooling down to room temperature, the nanoparticles were subsequently centrifuged and washed three times with ethanol and cyclohexane before drying in air at 70 °C. Thirdly, the three sizes of nanoparticles with volume concentration of 0.03% were dispersed into a type of vegetable insulating oil, the FR3 mechanized from Cargill, by ultrasonic dispersion, and they were tagged by sample A, B, and C, respectively; before electrical characterization, three nanofluids and the FR3 were dried at 85 °C under 50 Pa for 72 h.

Material characterization: The morphology of the Fe_3O_4 nanoparticles was characterized with a JEOL JEM-2100F high resolution transmission electron microscope (TEM). The X-ray diffraction (XRD) pattern was obtained by using a powder X-ray diffraction meter that equipped with a rotating anode and a Cu-Kα radiation source. The scan step was 0.02°. The AC breakdown voltage of the nanofluids was measured in accordance with the IEC 60156 standard. Trapping characteristics of the nanofluids were tested with the TSC method.

3. Results and discussion

Fig. 1 shows the XRD results of typical Fe_3O_4 nanoparticle according to [6] and three different sized samples were obtained by high temperature decomposition method. It can be seen from the figure, the XRD patterns of Fe_3O_4 nanoparticle near 20° have a very wide amorphous peak, this is because the nanoparticles surface coated with a large number of oleic acid. The sharp peaks of different samples show reveal that the nanoparticles have high crystallinity. According to JCPDS card No. 65-3107, the 2θ values of 30.1°, 35.5°, 43.1°, 56.9°, and 62.6° are signatures of (220), (311), (400), (511) and (440) crystal face for Fe_3O_4, respectively. Therefore, these XRD patterns may be indicative of the spinel structure of the Fe_3O_4 nanoparticles.

The morphologies of the three nanoparticle classes and the schematic of the core–shell nanoparticles are shown in Fig. 2. The nearly spherical Fe_3O_4 nanoparticles (Figs. 2a–c) are monodisperse; each nanoparticle consisting of two regions—the dark central-core is the Fe_3O_4 crystal and the surrounding layer is a low density shell of oleic acid. Covalent binding between oleic acid and Fe_3O_4 crystals prevents agglomeration of Fe_3O_4 nanoparticles and also improves the compatibility between the nanoparticles and the vegetable insulating oil. We selected two attached Fe_3O_4 nanoparticles and measured their surfactant thickness d and crystal size $2a$ (Fig. 2d). The surfactant thickness d is half of the distance between the crystals of the two attached nanoparticles. Fig. 2 shows that
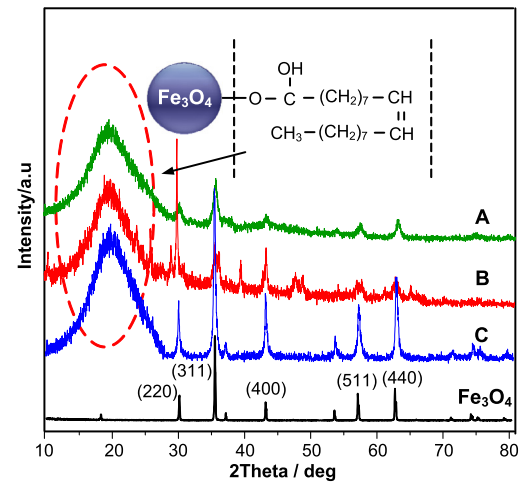

Fig. 1. XRD patterns of pure Fe_3O_4 and Fe_3O_4 nanoparticle at different reaction time: (A) 24 h, (B) 48 h and (C) 72 h.

the thickness of the surfactant shell changes from 1.5 to 1.4, and 1.8 nm; the Fe_3O_4 crystals grow from 13.7 to 23.0 and 40.7 nm as the reaction time increases from 24 to 72 h. The high magnification TEM images (inset in top right) clearly show the border between surfactant shell and Fe_3O_4 crystal. Meanwhile, we define the surfactant thickness ratio as $p = d/2a$. It decreases as reaction time increases.

Fig. 3 presents the AC breakdown voltage of the nanofluids and the FR3 oil. The measurement result of the FR3 oil is marked as the sample with nanoparticles in size of 0 nm added. The AC breakdown voltage of nanofluids increases as a function of nanoparticle size. That is, the AC breakdown voltage of nanofluids increases by 24.5% from 55.1 kV for the FR3 fluid to 68.5 kV for the nanofluid C containing 40.7 nm Fe_3O_4 nanoparticles. The breakdown strength increases for nanofluids with a smaller thickness ratio of surfactant.

The breakdown mechanisms of nanofluids are related to the trapping depth of the nanofluids. In Fig. 2, it is found that the surfactant is coated on the nanoparticle surface and the surfactant volumetric concentration is 40% over the complete nanoparticle volume (Fig. 2a). The surfactant may critically influence the trapping depth of the nanofluids. In order to understand the effect of surfactant on the trapping depth of nanofluids, the trapping depth of nanofluids were measured by TSC and calculated by nanoparticle polarization model.

The TSC curves of the pure FR3 oil and the three different sized vegetable oil-based nanofluids were tested [5] and shown in Fig. 4; we calculated the trapping depth [15] of the FR3 oil and the three sized nanofluids equal to 0.353, 0.403, 0.569, and 1.111 eV, respectively. These results indicate that the nanoparticles improve the trapping depth of the vegetable insulating oil. The trapping depth of the three nanofluid samples increases as the nanoparticle size grows up.

We used the nanoparticle polarization model presented in [9] to calculate the trapping depth of the vegetable insulating oil-based nanofluids. The model supposes a spherical nanoparticle (size $2a$, relative dielectric constant $\varepsilon_2 = 20$) in an insulation material (relative dielectric constant $\varepsilon_1 = 3.2$) and an external electric field ($E_0 = 4$ kV/mm) applied in the direction of the x-axis. Polarization charges gather on the surface of the nanoparticle: the positive dipole surface charge is induced between the angle range $-\pi/2 < \varphi < \pi/2$, and the negative dipole surface charge is induced between the angle range $\pi/2 < \varphi < 3\pi/2$ (see Fig. 5). The electric potential distribution, $V(r, \varphi)$, induced by the dipole surface charge density, is as: