

Trapping and scattering effect of charge carriers on impulse breakdown characteristics of nano-fluids

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Propylene carbonate (PC)-based nano-fluids (NFs), containing only 2 ppm TiO₂ nano-particles, exhibit more than 60% higher negative impulse breakdown voltage than that of base liquid. It is found that the resistance of the test gap containing PC remains basically invariable when subjected to high amplitude voltage before the development of electrical breakdown. However, for the NF case, the resistance increases by a factor. Moreover, compared with PC, the streamers in NFs are more complex branched. These experimental results indicate that the charge carriers in NFs can be effectively captured and scattered by nano-particles, which is verified by means of the thermally stimulated current method.

1. Introduction: Propylene carbonate (PC), which has been used as a dielectric in high-performance lithium batteries, shows appealing prospects in the compact pulsed power sources because of its large permittivity, high dielectric strength and broad operating temperature range [1–3]. Compared with the traditional polar liquids used in pulse forming line as an energy storage medium, such as deionised water and water/ethylene glycol mixtures [4–9], PC owns relatively high chemical stability and can keep the resistivity above 10 MΩ cm for more than six months in pulse forming line, which can be used for microsecond charging with less energy loss [10, 11].

Up to now, various favourable results in electrical engineering fields have shown that by adding nano-particle suspensions into transformer oil, both alternating current and direct current (DC) breakdown strength of the base liquid can be enhanced [12–14]. Our recent work has also found that, in a short (1 mm) gap with a quasi-uniform field, nano-fluids (NFs) exhibit significantly improved dielectric performance and increased breakdown stability under microsecond pulse [15–17]. Nevertheless, these results are inconsistent with conventional wisdom believing that insulating performance of a dielectric liquid is strongly related to its purity, and there is no consensus regarding the mechanism for the modification effect of nano-particles on breakdown characteristics of the matrix to date. Hwang has established an electron scavenging model demonstrating that nano-particles in liquids can capture free fast electrons and convert these fast electrons to much slowly moving charged carriers [18]. Lv has proposed that nano-particles in the matrix can both lower the shallow trap energy level and increase the trap density. The dielectric strength of the matrix can thus be enhanced due to the rapid transfer of charge carriers via the trapping and de-trapping process in shallower traps [19]. Although these two mechanisms can be used to explain some experimental results, the essential attributes of traps and their effects on electrons' transportation are not very clear by now. Therefore, we investigated the basic charge carriers' transportation processes in PC and NFs, and then discussed the trapping and scattering effect of charge carriers on the breakdown voltages and streamer structures based on the electronic energy band theory.

2. Experiments: Due to the extremely large surface area/particle size ratio, the outsourcing TiO₂ nano-particles were always

agglomerated. So we utilised the γ -aminopropyltriethoxysilane coupling agent to modify them. Fig. 1a illustrates a transmission electron microscopy image of nano-particles dispersed in PC, with the size ranging from several nano-metres to several tens of nano-metres. It is obvious that the aggregation effect between the nano-particles has been largely weakened by the surface modification of a silane coupling agent and these nano-particles were homogeneously dispersed in PC. The particle size distribution is shown in Fig. 1b. NF samples containing 2 ppm (part per million) nano-particles were tested in this study.

The experimental set-up is shown in Fig. 2 and the pulsed power source, which generates a microsecond pulse, has been described in detail in previous publications [15]. The test cell consists of a stainless steel plane electrode with a diameter of 4 cm, serving as the anode and a pin electrode with a conical point with a diameter of about 230 μ m, serving as the cathode. The gap distance was adjusted to be 5 mm during testing. The voltage across the gap was measured by using a high-voltage probe (Pintech, 1000:1, 220 MHz) on the source side of the test gap and the current flowing through the gap was measured by using a Pearson Current Monitor (Model 6585, 1 V/A, 200 MHz) on the ground side. The test cell has a quartz window for a four-channel high speed framing camera recording the emission light of streamers.

3. Results and discussions: Fig. 3a illustrates the example of the temporal development of the voltage across the test gap and the current, which is the sum of displacement and resistive current. When the voltage approaches the negative maximum value, its first-order derivative equals to zero and the measured current corresponds to the resistive current. By increasing the voltage applied to the primary capacitor, we can get a different negative maximum voltage of the test gap until breakdown. Fig. 3b shows the resistive current–voltage characteristics for PC and NFs. It is obvious that the resistive current through the PC test gap is linearly increasing with the voltage up to the breakdown voltage of about –31 kV. As for NFs, the resistive current increases linearly with the voltage until –25 kV, and this is consistent with that of PC. However, at voltages exceeding –25 kV, the current remains basically invariable up to the breakdown voltage of about –50 kV. Compared with PC, the NFs possess more than 60% higher breakdown threshold and the double resistance before the

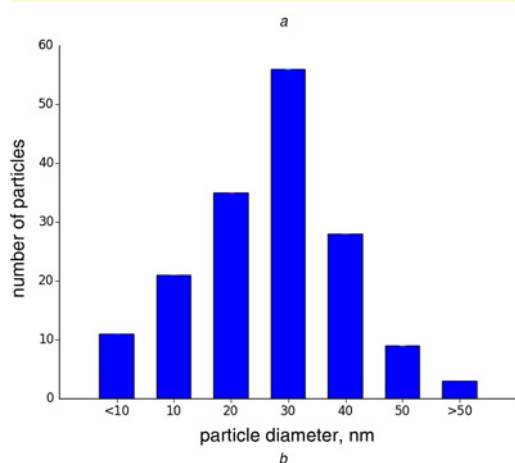
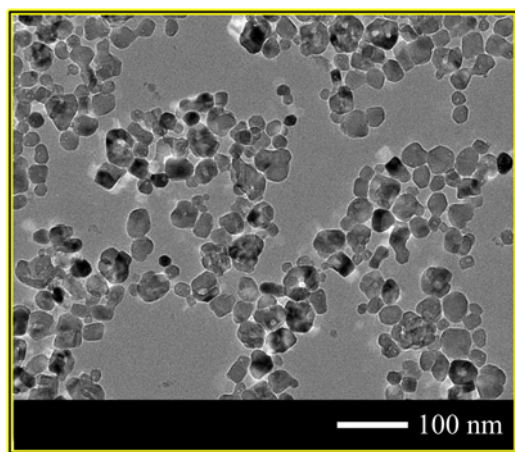


Fig. 1 *TiO₂ nanoparticles used in this experiment*
a Transmission electron microscopy image of γ -aminopropyltriethoxysilane coupling agent-grafted TiO_2 nanoparticles dispersed in PC and
b Particle size distribution

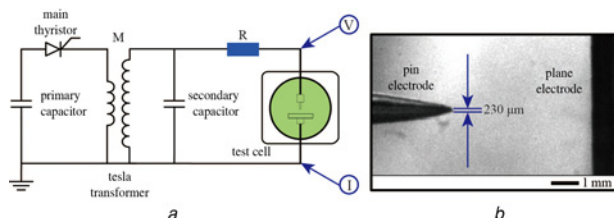


Fig. 2 *The experimental set-up*
a Circuit diagram for pulsed voltage and current measurement device
b Pin-plane electrode configuration

development of electrical breakdown, which can be caused by the nano-particles' trapping or scattering effect on charge carriers.

Fig. 4 shows the luminous streamers initiating from the pin electrode, propagating and touching the plane electrode in PC and NFs' gap, respectively. There is a single luminous streamer crossing the PC gap. However, streamers in NFs tend to be more complex branched, indicating high-energy charge carriers can be effectively scattered by nano-particles.

Based on the above favourable experimental results, it is desirable to establish a NF dielectric-based coaxial pulse forming line system. Since NFs possess much larger breakdown voltages than that of PC, the maximum energy storage density of the NF-based pulse forming line can be increased. This means in order to generate the same pulse power, the volume of pulse forming line using NFs as the energy storage medium can be reduced.

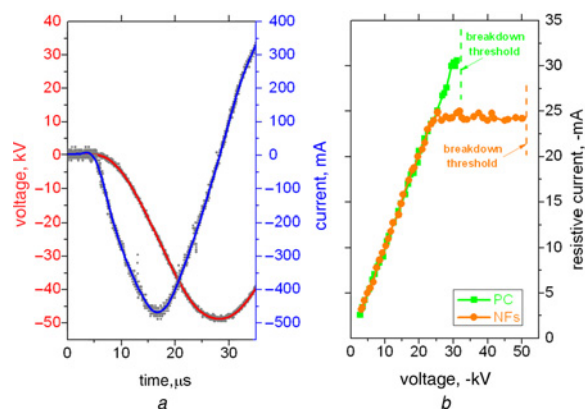


Fig. 3 *The experimental results*
a Test cell voltage and current measured in experiment (dots) and filtered traces (solid curves)
b Pre-breakdown resistive current–negative maximum applied voltage characteristics for PC and NFs

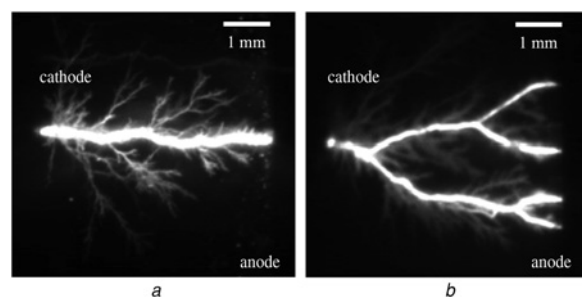


Fig. 4 *Streamers generated in*
a PC
b NFs for the pin-plane electrode configuration

To investigate the nature of charge carrier traps in the PC and NFs, the thermally stimulated current (TSC) method was used. The set-up procedure of TSC has been described in other publications [20, 21] and we will only provide some essential facts on the operating procedure. The test samples had a thickness of 100 μm and the temperature of the chamber was 25°C as the original state. At first, a 10 V/mm DC electric field was applied to the samples for 20 min for polarisation. Then the samples were cooled rapidly to -70°C with the polarisation voltage still applied. After that, polarisation voltage was removed. In the meantime, the circuit was shorted for 2 min to release the free charge carriers in the samples. Finally, the thermally stimulated depolarisation current could be measured using a sensitive galvanometer by increasing the temperature linearly to $+140^\circ\text{C}$, as shown in Fig. 5. Both the TSC profiles of PC and NFs contain a negative peak occurring at 30°C with a current value around -35 nA. Also, for NFs, the TSC curve contains another peak at 110°C with a current value -250 nA. Since the peak value relates to the maximum trap density, the experimental results indicate that the introduction of TiO_2 nano-particles into the PC matrix produces much larger trap densities. The trap centre of PC can be calculated as -0.3 eV by analysing the half peak width of the TSC curve [19], and for NFs, trap centres are -0.3 and -0.78 eV.

Charge carriers will arise by injection at the electrode or dissociative ionisation of liquid molecules [22, 23]. When an electron has been attached to the PC molecule, the ionised states will be modified by the collective polarisation of the surrounding PC molecules. Fig. 6 illustrates the electronic energy states in PC and NFs, in which the energy levels are broadened into Gaussian distributions $P(W)$ by thermal agitation. According to TSC results, charge

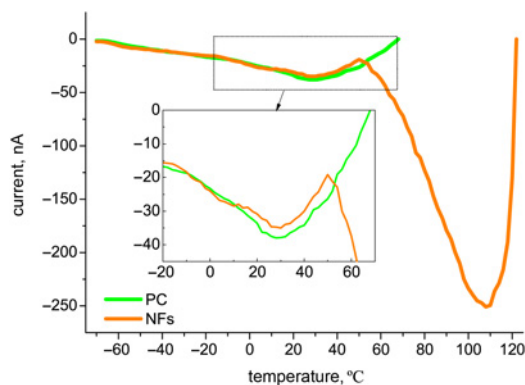


Fig. 5 Thermally stimulated current results of PC and NFs

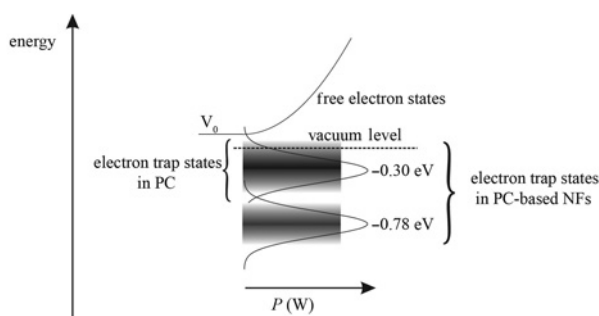


Fig. 6 Electronic energy states in PC and NFs

carriers become trapped at states of -0.3 eV in PC, while nanoparticles can trap electrons at the states around -0.78 eV. Under high amplitude electrical stress, the drift velocity of the charge carrier can exceed the thermal velocity and the energy acquired from the field can be dissipated by stimulating various vibrational modes of PC molecules, which will lead to phase instabilities and the formation of localised low-density regions. The scattering rates of charge carriers will fall in low-density regions and the mean-free paths will become larger. Then the electric discharge can be initiated. For NFs, the charge carriers can effectively be trapped due to the much deeper trap sites and larger trap densities introduced by nano-particles. In the meantime, charge carriers can be scattered and reflected by the boundaries of nano-particles, and the charge carriers' effective mean-free path will be greatly shortened. As a result, in order for charge carriers to acquire enough energy to generate a low-density region and to initiate breakdown in NFs, a much higher applied field is needed.

4. Conclusions: In summary, NFs consisting of TiO_2 nano-particles modified by a silane-coupling agent exhibit significantly enhanced dielectric performance. The resistive current through the PC test gap is linearly increasing with the voltage up to the breakdown voltage. On the other hand, for NFs, the resistive current increases linearly with the voltage until -25 kV, then the current remains basically invariable up to the breakdown voltage. What is more, streamers in NFs tend to be much more ramose. These experimental results indicate that charge carriers can be effectively trapped and scattered by nano-particles. Finally, we verify this idea by the TSC method showing that TiO_2 nano-particles producing much larger trap densities and deeper trap sites into the PC matrix. By the trapping and scattering effect, the formation of localised low-density regions can largely be inhibited and dielectric performances of NFs can thus be enhanced.

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6 References

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