Effect of surface modification of electrodes on charge injection and dielectric characteristics of propylene carbonate

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Abstract: Space charge injected into a liquid dielectric by an electrode under an impulse voltage causes the electric field to be distorted, which affects the dielectric’s insulation performance. In this study, the authors study the surface modification of three-electrode materials, namely aluminium, copper, and stainless steel, by sputtering of titanium dioxide (TiO2) based on magnetron sputtering. The breakdown voltage of propylene carbonate and the surface morphology of the electrodes before and after modification were examined. Furthermore, the distribution of the space charge injected into the propylene carbonate from the different electrode materials was also measured based on the Kerr electro-optic effect. These results indicate that the breakdown voltage of propylene carbonate increased by 7, 4, and 9% after surface modification of aluminium, copper, and stainless steel, respectively. After sputtering of TiO2, micro-grooves on the surface of the three-electrode materials became smooth, and the surface roughness decreased, which changed the barrier height of the solid–liquid interface. The space charge injection mode of the three-electrode materials before and after surface modification was bipolar injection; however, the space charge injection amounts were markedly lower for the modified electrodes.

1 Introduction

Liquid dielectrics, having high dielectric breakdown strength, good dielectric recovery, and heat dissipation characteristics, are widely used in power equipment. In recent years, transmission voltage levels have increased, and requirements for liquid dielectric insulation performance are becoming more severe. The insulation performance of liquid dielectrics plays an important role in the safe and stable operation of power systems. Considerable research has been performed to further improve the dielectric strength of the liquid dielectrics. However, the complex mechanism of electrical breakdown in liquids is still not completely understood [1]. The key factor determining the impulse insulation performance of a liquid dielectric is its insulation properties and the effects of space charge during discharge. At present, modification of the interactions of the dielectric with the electrode surface is a commonly used method for controlling liquid insulation performance. These approaches including directly altering the physical and chemical properties of liquid dielectrics such as through the use of nanoparticle modified liquid dielectrics [2–4], which can introduce potential wells or holes, capture fast-moving electrons, and inhibit the development of streamers [5]. Besides, through an indirect action on the space charge injection, the surface of the electrode material can also be modified to change the surface chemical characteristics and physical morphology of the electrode and inhibit charge injection [6], and thus change the impulse insulation characteristics. Notably, nanoparticles easily form deposits and do not easily form stable nanofluids for power grid main equipment. However, electrodes inject a certain amount of space charge into a liquid dielectric under the action of external voltage, which disrupts the distribution of the original electric field, affecting the development of streamers. This effect and has an important influence on the insulation performance of the liquid [7].

Many researchers have attempted to control the impulse insulation properties of liquid dielectrics in terms of both the electrode material and its surface modification. Selection of appropriate electrode materials can inhibit charge injection, thus improving the insulation performance of the liquid [8]. Charge injection is related to the interfacial barrier between the electrode material and the liquid dielectric [9], which is mainly affected by the electrode material [10–12], the surface morphology of the electrode [13–15], the properties of the liquid dielectric, and the distance between the electrodes [16]. Changing the electrode surface conditions through surface modification also affects the work function of the metal electrode [17], possibly lowering the work function of the metal electrode to increase the possibility of charge injection [18–20]. Therefore, charge injection can be inhibited by appropriate modification of electrode materials, and the liquid insulation performance can be improved.

Surface modification technology can inhibit the accumulation of surface charges by changing the surface chemical properties and physical morphology of the electrode material, thereby improving the withstanding voltage characteristics of insulating materials [21–23]. Common methods include dielectric barrier discharge [15], direct fluorination [24], and vacuum magnetron-sputtering thin film deposition [25]. Liu et al. effectively reduced the electron field emission and ionisation of an electrode by coating the electrode surface with an insulating film, which enhanced the dielectric breakdown strength [26]. He et al. used a high-vacuum magnetron-sputtering method to sputter a chromium (III) oxide (Cr2O3) insulating film on the surface of epoxy resin and a pure copper sheet to inhibit the amount of charge injected from the electrode and reduce the surface charge level [25]. Shao and Wang et al. used a dielectric barrier discharge plasma treatment to deposit titanium dioxide (TiO2) film on the surface of copper [22, 23]. They found that the surface roughness of the electrode was considerably reduced and the interface electric-field distortion was improved, which inhibited air micro-discharge at the surface of the electrode. At present, surface modification technologies are mature, in particular magnetron-sputtering deposition technologies, which have the advantages of a high film formation rate and large area uniform film formation [27–29]. These methods have been widely studied and show great promise as an approach to surface modification of media. However, this method has seldom been examined for improving dielectric impulse strength. Therefore, the surface modification of electrode materials by magnetron-sputtering technology requires further study. Furthermore, there is
a need for a greater understanding of the space charge injection characteristics of electrodes into liquid dielectrics to improve the mechanism of influence of liquid insulation performance.

TiO$_2$ is a transition metal oxide with a high refractive index, excellent electrical properties, and high chemical stability. It is also a wide band gap inorganic semiconductor material [30] with a high work function and we considered it to be a suitable dielectric film for suppressing charge injection in this paper. The equipment used for magnetron sputtering of TiO$_2$ enables reproducible results, and can be used to prepare crystals with good crystallinity at low temperatures. The system is widely used in material modification [31].

In this paper, the Kerr electro-optical effect is only apparent in a large electric field or a liquid having a large Kerr constant. Therefore, the propylene carbonate, in which a large Kerr constant $B$ (about $1.2 \times 10^{-12}$ m$^2$/V$^2$) and is a highly polar liquid medium ($\varepsilon_r$ = 69), has been selected as the liquid dielectrics. Moreover, propylene carbonate is widely used, and it can be used as an excellent medium for high-energy batteries and capacitors in the electronics industry. The surfaces of aluminium, copper, and stainless steel were modified by vacuum magnetron sputtering. The change of surface morphology of the electrodes and the breakdown strength of the liquid before and after electrode modification was determined. The spatial electric field and space charge distribution of the liquid dielectric before and after modification were measured based on the Kerr electro-optical effect. On the basis of the measurement results, we propose a mechanism through which the electrode surface modification suppresses charge injection.

2 Testing procedure

2.1 Test sample

Three types of electrodes, namely aluminium, copper, and stainless steel, were selected as the test electrodes. Two groups were selected for each electrode material to compare the impulse insulation properties of propylene carbonate before and after surface modification of each electrode material. There are three kinds of electrode materials, and each electrode material has at least four samples. Before the modification, a polishing machine was used to polish the electrodes, and the surface smoothness of the parallel plate electrodes was consistent. Three pairs of aluminium, copper, and stainless-steel parallel plate electrodes were modified with a magnetron-sputtering machine. The target used for the experiments was 76.2 mm in diameter, 3 mm thick, anatase type, and 99.99% pure TiO$_2$. To ensure uniform heating of the target during sputtering, and avoid cracking, the backside of the target was welded with a copper plate, ~2 mm thick, with indium, as shown in Fig. 1. The sputtering duration was 45 min at a sputtering power of 300 W under an ultra-high-vacuum environment of $4 \times 10^{-1}$ Pa. High-purity argon (Ar) was used as the sputtering gas and the gas flow rate was 46 sccm. The film formation rate measured in the experiment was within the range of 0.2–0.7 nm, and the film thickness was about 100 nm. The plasma generation and film deposition during sputtering are illustrated in Fig. 1. Electrons are accelerated under the action of an electric field and collide with Ar atoms to generate a large amount of Ar$^+$ ions and electrons, producing a uniform glow discharge. The electrons fly toward the substrate, and the Ar$^+$ ions accelerate the bombardment of the TiO$_2$ target under the action of the electric field and sputter a large amount of TiO$_2$ neutral target particles, which are deposited on the substrate to form a film. Since the plasma generated by the glow discharge has good uniformity and reproducibility, modification of the electrode can be achieved consistently. After modification, the electrodes were removed and their surface morphology was analysed.

2.2 Impulse breakdown test

The impulse-voltage generator and space charge measurement system were built in this paper, according to the test standard of impulse breakdown voltage (IEC60897), as shown in Fig. 2. The impulse-voltage testing system was composed of an impulse-voltage generator generating platform, the test sample, and the measuring circuit. The standard operating impulse voltage of negative polarity (250/2500 μs) was used. The test sample was placed in a Kerr cell with an inner diameter of 16 cm and height of 30 mm. The outer wall of the Kerr cell was made of stainless steel and the inner wall was 5 mm thick polytetrafluoroethylene. The electrode was fully immersed in liquid. The upper plate was connected with a high voltage by a highly adjustable copper rod. The lower plate was connected to the ground potential by a fixed copper rod. The measurement part of the signal line was connected to the signal terminal of the capacitance divider, which is linked with the oscilloscope through matching resistance. The final breakdown waveform was recorded by the oscilloscope.

![Fig. 1 Schematic illustration of magnetron sputtering](image1)

![Fig. 2 Experimental setup used to measure the breakdown voltage and space charge in liquid dielectrics](image2)
impulse breakdown voltages for electrodes samples with a 3 mm gap in propylene carbonate were measured by the step-stress test. To ensure the accuracy of the breakdown test results, at least five pulses were applied from the initial voltage before each breakdown, the same voltage is applied at least three times, and the interval between tests was at least 2 min.

2.3 Space charge measurements

To investigate the effect of low-temperature plasma-modified electrode materials on charge injection of propylene carbonate from the perspective of space charge, we measured the distribution characteristics of the electric field and space charge before and after surface modification of the electrode under switching impulse voltage. The measuring platform consisted of three parts: an impulse-voltage circuit system, optical platform, and light intensity measurement system, as shown in Fig. 2. The system produced a secondary electro-optic effect when polarised light passed through the Kerr cell. A high-speed charge-coupled device recorded the light intensity signal to a computer. We used a helium–neon laser as the light source, and the secondary electro-optic effect when polarised light passed through polarisers and the Kerr dielectric was measured. Here, the electric-field direction has a quadratic relationship with the magnitude of the applied electric field and space charge. The gap between the plates in the space charge measurement experiment was 3 mm. The electric-field curves at different positions between the plates under the applied voltage can be determined by the photoelectric conversion method. The charge density between the electrodes is inversely calculated by the Poisson equation

\[ \rho(x) = \varepsilon_0 \varepsilon I \frac{dx}{dx} \]  

where \( \varepsilon_0 \) and \( \varepsilon_1 \) are the vacuum dielectric constant and the relative dielectric constant, respectively, and \( x \) is the gap distance between the plates. According to (6), the distribution of space charge at different positions between the plates can be determined.

3 Results and discussion

3.1 Impulse breakdown test results

Fig. 3 shows the breakdown voltage of propylene carbonate under different electrode materials before and after sputtering TiO\(_2\). Different work functions of aluminium, copper, and stainless steel result in different barrier heights at the interface between the plate and liquid. Therefore, the ability of three-electrode materials to inject space charge into the liquid differed. The highest breakdown voltage of propylene carbonate was measured under stainless steel, followed by copper, and finally aluminium. The breakdown properties of the three-electrode materials modified by sputtered TiO\(_2\) in propylene carbonate improved to varying degrees. The breakdown voltages of the liquid for the aluminium, copper and stainless-steel electrodes increased by 7, 4, and 9\%, respectively. The greatest increase in the insulating breakdown voltage was measured for the stainless-steel electrode and the lowest for the copper electrode. These results suggest that different mechanisms might operate for the different metal electrodes with surface sputtered TiO\(_2\). We further analysed the mechanism by which the surface modification of the electrode materials affected charge injection into the liquid from the distribution characteristics of the electric field and space charge before and after sputtering TiO\(_2\).

3.2 Electrodes surface topography test results

To examine the surface morphologies of the three kinds of electrodes, we used an asylum research molecular force probe 3D Bio (MFP-3D-BIO) atomic force microscope to obtain the three-dimensional surface morphology and roughness of the electrodes before and after surface modification. Figs. 4 and 5 show the surface morphology of the three electrodes before and after modification. Table 1 shows the roughness changes before and after modification. Fig. 4 and Table 1 indicate that differences in the surface morphologies of the different electrode materials despite the same polishing method and parameters being used. The

According to the inverse function of (3), a relationship between \( E/E_m \) and \( I/I_0 \) is obtained, when the relative light intensity is weakly enhanced

\[ E/E_m \left[ \frac{n + 2}{\pi} \arcsin\left(\frac{I}{I_0}\right)^{1/2} \right] = \frac{1}{2} \]  

(4)

When the relative light intensity decreases from strong to weak

\[ E/E_m = \left[ \frac{n + 2}{\pi} \arcsin\left(\frac{I}{I_0}\right)^{1/2} \right] \]  

(5)

From (4) and (5), the electric field between plates can be determined.

Since the applied voltage affects injection of space charge. To study the change of the charge injection amount of the three kinds of electrode materials before and after the surface modification, the applied voltages should be kept unchanged. Moreover, the liquid is required to not breakdown and appears significant Kerr effect. A negative standard operating impulse voltage had applied voltage to the three-electrode materials before and after modification and maintained at 28 kV when measuring variations of the electric field and space charge. The gap between the plates in the space charge measurement experiment was 3 mm. The electric-field curves at different positions between the gaps under the applied voltage can be determined by the photoelectric conversion method. The charge density between the electrodes is inversely calculated by the Poisson equation

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where \( \varepsilon_0 \) and \( \varepsilon_1 \) are the vacuum dielectric constant and the relative dielectric constant, respectively, and \( x \) is the gap distance between the plates. According to (6), the distribution of space charge at different positions between the plates can be determined.
The roughness of the electrode is one of the ways to represent the surface topography, the greater the roughness of the same electrode, the electrode will affect the breakdown voltage of the liquid [8]. The electrode material and the surface morphology of the aluminium electrode were 42.23 nm, whereas those of the copper and stainless-steel electrodes were, respectively, 31.08 and 26.91 nm. Hence, the roughness $R_q$ of the electrodes decreased in the order: aluminium > copper > stainless steel. The root mean square roughness $R_{aq}$ of the three-electrode materials also followed the same pattern. The impulse breakdown strengths of propylene carbonate with the three kinds of electrodes varied. We infer that the micro-morphology of the three electrodes varied, which caused the differences in the space charge injection ability among the three kinds of electrode materials. This result might also be attributed to the differences in the work functions of the three-electrode materials. Table 1 shows that the surface roughness $R_q$ of aluminium, copper, and stainless-steel electrodes after surface modification decreased to 31.72, 14.97, and 13.71 nm, respectively. The root mean square roughness $R_{aq}$ of the three-electrode materials also followed the same pattern. The results of the impulse breakdown test indicated that the breakdown strength of propylene carbonate increased to varying degrees after surface modification, owing to the change of the surface morphology of the electrode. Since the other parameters of the impulse breakdown test were unchanged before and after surface modification, we consider that the plasma produced by magnetron sputtering bombarded the electrodes and deposited on the surface of the electrodes, resulting in gentle micro-grooves of the three types of electrodes. Similar results have been reported for surface sputtered Cr$_2$O$_3$ thin films on epoxy resin samples [25]. After sputtering, the surface roughness of the epoxy resin samples decreased. Moreover, the surface deposited film inhibited charge injection. The surface roughness of these electrode materials decreased to different degrees owing to the deposition of TiO$_2$ film on the electrode surface.

| Electrode materials | Before surface modification $R_q$, nm | $R_{aq}$, nm | After surface modification $R_q$, nm | $R_{aq}$, nm |
|---------------------|-----------------|--------------|-----------------|--------------|
| aluminium           | 57.95           | 42.23        | 37.89           | 31.72        |
| copper              | 40.07           | 31.08        | 20.02           | 14.97        |
| stainless steel     | 32.17           | 26.91        | 17.83           | 13.71        |

Fig. 4 Surface morphology of the electrode before surface modification
(a) Aluminium, (b) Copper, (c) Stainless steel

Fig. 5 Surface morphology of the electrode after surface modification
(a) Aluminium, (b) Copper, (c) Stainless steel

Fig. 6 Electrode topography after breakdown test

The roughness of the electrode is one of the ways to represent the surface topography, the greater the roughness of the same electrode material, the lower the breakdown voltage. Moreover, the different work functions of electrode materials will affect the charge injection. Among the three-electrode materials, stainless steel has the highest work function (5.05 eV), followed by copper (4.5 eV), and aluminium (4.2 eV) [33]. Moreover, roughness will have a certain impact on the work function, which has an influence on the interface barrier; therefore, the variation law of this roughness is the same as the variation law of the breakdown voltage.

Fig. 5 and Table 1 indicate that the micro-grooves on the surface of the three-electrode materials became less pronounced after surface modification, owing to the collision of neutral particles on the surface of the electrodes and deposition of thin films. The plasma produced by magnetron sputtering bombarded the electrodes and deposited on the surface of the electrodes, resulting in gentle micro-grooves of the three types of electrodes. Ultimately, the impulse insulation strength of olefin esters increased for all electrode materials. In our coating equipment, there is a film thickness measuring instrument, and the film thicknesses of the three kinds of electrodes were measured to be about 100 nm, thicknesses of the coating may affect the interfacial charge behaviour of the metal liquid, the cross-section of the TiO$_2$ will be measured in our future work. Next, we further analysed the mechanism from the perspective of space electric field and space charge.

Electrode topography after breakdown test was obtained with a scanning electron microscope as shown in Fig. 6. After the breakdown test, the breakdown locations of the electrode surface will show the melting phenomenon. At the other breakdown material, the lower the breakdown voltage. Moreover, the different work functions of electrode materials will affect the charge injection. Among the three-electrode materials, stainless steel has the highest work function (5.05 eV), followed by copper (4.5 eV), and aluminium (4.2 eV) [33]. Moreover, roughness will have a certain impact on the work function, which has an influence on the interface barrier; therefore, the variation law of this roughness is the same as the variation law of the breakdown voltage.

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locations, the coating on the electrode surface shows blasting condition. However, the coating on the electrode surface is intact at the locations without breakdown.

3.3 Electric-field and space charge distribution

The distributions of electric field and space charge before and after sputtering of TiO$_2$ onto three electrodes were measured based on the Kerr electro-optical effect. Figs. 7 and 8 show electro-optical field diagrams of propylene carbonate before and after modification of the different electrode materials. The light-dark interference fringes in the pattern are equipotential lines. From Figs. 7 and 8, we can clearly see interference fringes between the light and dark parts of the plates, which indicate a certain degree of distortion of the electric field in the propylene carbonate between the electrodes. The fringes in the electro-optic intensity diagrams of the three sets of electrode materials were not the same and also varied over time. After surface modification of the electrode, we found that the number of stripes in the propylene carbonate decreased.

Figs. 9 and 10, respectively, show the spatial electric-field distribution of propylene carbonate before and after surface modification when the three electrodes are applied with operating impulse voltage. Since the electrodes are plate electrodes, the electric field between the plates is an approximately uniform electric field, and the electric field in the horizontal direction does not change much. Therefore, we can think that the electric field in the vertical direction can represent the electric field between the plates. These data were obtained from the vertical direction of the electro-optic intensity diagram (white lines in Figs. 7 and 8). Table 2 shows the electric-field distortion rate of propylene carbonate between plates before and after surface modification. Equation (7) was used to calculate the electric-field distortion rate ($D$) in the liquid dielectric

$$D = \left| E - E_{\text{avg}} \right|_{\text{max}} / E_{\text{avg}} \times 100\%$$

where $E_{\text{max}}$ is the maximum electric field and $E_{\text{avg}}$ is the average electric field between the electrodes. Fig. 9 shows that the electric-field distribution between the three electrodes had different degrees of distortions at different times, and the electric-field distortion degree of different electrode materials at the same time was obviously different. The electric-field distortion between electrodes occurred mainly at the cathode and anode.

According to Fig. 9 and Table 2, the degree of the electric-field distortion increased first and then decreased over time. The
electric-field strength was low at 150 μs, and the space charge of the propylene carbonate injected from the electrode was small such that the electric-field distortion rate was relatively low. At longer times, the electric-field strength also increased, and the space charge accumulated and transferred into the liquid, resulting in an increase in the charge of the propylene carbonate; hence, the spatial electric-field distortion increased. However, after 900 μs, the electric field decreased to a certain extent, and the space charge injected into the liquid by the electrode was markedly smaller than the recombination, transfer, and dissipation of the space charge in the liquid such that the space charge and the distortion of the electric field decreased.

The electric-field distortion rate of the three electrodes after surface modification decreased to some extent at the same points (Fig. 10 and Table 2). Nevertheless, the times at which the electric-field distortion rate reached their maximum values were the same before surface modification. For aluminium, the electric-field distortion rate of propylene carbonate at the electrode reached a maximum at 700 μs, and both copper and stainless steel reached their maxima at 650 μs. The electric-field distortion after modification of the electrode surface mainly occurred near the cathode and anode. The decrease of the electric-field distortion rate indicates that the space charge injection decreased after the surface modification, which is consistent with our examination of the electrode surface topography. Thus, the surface modification reduced the roughness of the post-electrode electrode, which influenced the interface barrier height between the electrode and liquid. The space charge of the injected liquid and the distortion rate of the electric field were decreased.

Figs. 11 and 12 show the space charge distribution of propylene carbonate, with three types of electrodes applied with an operating impulse voltage before and after surface modification. The space charge of aluminium, copper, and stainless-steel electrodes in propylene carbonate had a bipolar injection mode, as shown in Fig. 11. That is, a negative charge is injected near the cathode and a positive charge is injected near the anode. The amounts of space charge injected by different electrode materials and time point were different. For the aluminium electrode, the space charge injected into the propylene carbonate was as low at 150 μs, and the charge mainly concentrated near the cathode and anode, at values of −0.54 and 0.42 C/m³, respectively, whereas the charge in the middle of the plate gap was almost zero. At 250 μs, the space charge density of the cathode and anode reached −1.50 and 1.02 C/m³, respectively, and the amount of charge in the middle of the plate gap remained small, indicating that the space charge injected by the electrode accumulated near the cathode and anode. The charge recombination and dissipation rate were less than the charge injection rate. At 500 μs, a large amount of charge accumulated in the middle of the plate gap, and the amount of charge near the plate decreased slightly, indicating that charge was transported from the cathode and anode to the middle under the action of the electric field. Charge transport requires a certain amount of time but has already completed a distance between the plates of 500 μs. A large number of heterogeneous charges recombine in the middle of the plate gap, up to 900 μs. At 1200 μs, because the electric field

| Table 2 | Distortion rate of the electric field in propylene carbonate before and after surface modification |
|-----------------|---------------------------------|
| Electrode materials | Distortion rate |
| | 150 μs, % | 250 μs, % | 500 μs, % | 650 μs, % | 700 μs, % | 900 μs, % | 1200 μs, % | 1500 μs, % |
| aluminum before surface modification | 2.60 | 6.45 | 14.40 | 19.42 | 23.65 | 18.81 | 11.71 | 2.13 |
| copper | 1.41 | 6.61 | 17.83 | 26.69 | 23.65 | 15.57 | 10.56 | 2.87 |
| stainless steel | 2.04 | 6.41 | 16.44 | 18.74 | 15.08 | 14.60 | 11.37 | 2.52 |
| aluminum before surface modification | 1.02 | 5.67 | 9.77 | 10.23 | 14.15 | 9.34 | 7.30 | 1.34 |
| copper | 1.02 | 6.08 | 13.21 | 14.97 | 11.12 | 9.24 | 1.99 | 1.20 |
| stainless steel | 1.25 | 6.29 | 13.43 | 17.68 | 14.21 | 11.32 | 9.16 | 1.32 |

Fig. 9 Electric-field change distribution of propylene carbonate before surface modification (a) Aluminium, (b) Copper, (c) Stainless steel

Fig. 10 Electric-field change distribution of propylene carbonate after surface modification (a) Aluminium, (b) Copper, (c) Stainless steel
decreases, the charge injections of the cathode and anode are reduced, and the charge in the middle of the plate gap is also substantially recombination such that the amount of charge in the plate gap is markedly reduced. At 1500 μs, the charge density decreased to <0.1 C/m³, for both the cathode and anode and the gap between the plates.

The changes in space charge in propylene carbonate for the copper and stainless-steel electrodes were similar to that of the aluminium electrode. However, the time points at which the charge density reached its maxima were slightly different. The aluminium and copper electrodes had the highest charge density at around 650 μs and the stainless-steel electrode reaches the maximum at ~500 μs. The charge is mainly distributed near the cathode and anode. Charge injection of the same polarity optimises the electric field at the middle of the gap, before penetrating the whole gap, the electric field near the plate is weakened. This effect suppresses the initial stage of discharge and increases the difficulty of discharge.

As illustrated in Fig. 12, the space charge of aluminium, copper, and stainless-steel electrodes in propylene carbonate after surface modification is also induced by bipolar injection. The charge injection mode did not change; however, the amounts of charge injection at the same time points were lower, and the space charge of propylene carbonate between the plate gaps decreased. This result indicates that the surface modification by magnetron sputtering plasma layer effectively suppressed charge injection. The effects of different electrode materials treated by a magnetron-sputtering plasma layer on charge injection and impulse insulation characteristics of liquid dielectrics are related to properties of the liquid and electrodes including the properties of the liquid, which are related to the type of liquid, impurities, and gas contents. The characteristics of electrodes are related to the electrode material, shape, and surface conditions. Sputtering a TiO₂ film onto the surface of metal electrodes can influence the surface of the electrode, which affects the interface barrier height between the electrode and liquid dielectric [36, 37] and the ability of the electrode to inject space charge into the liquid. Thus, the electric-field distribution of the gap between the plates is changed.

4 Effect of electrode surface modification on impulse insulation performance of liquid dielectrics

Impulse breakdown testing results indicated that the breakdown voltage of propylene carbonate improved after surface modification of aluminium, copper, and stainless-steel electrodes. According to the results of electrode morphology tests, the roughness of the electrodes improved considerably after surface modification. Space charge measurements, which indicate the distribution of the electric field and space charge for the modified electrodes, showed temporal and spatial variations. We analysed the effects of surface modification of electrodes on charge injection and impulse insulation characteristics of liquid dielectrics.

The energy of electrons generated by magnetron sputtering in a low-temperature plasma is generally 1–10 eV. This modification only involves the surface of the material and does not affect the properties of the substrate [35]. Studies have shown that space charge injection of a liquid is related to properties of the liquid and electrodes including the properties of the liquid, which are related to the type of liquid, impurities, and gas contents. The characteristics of electrodes are related to the electrode material, shape, and surface conditions. Sputtering a TiO₂ film onto the surface of metal electrodes can influence the surface of the electrode, which affects the interface barrier height between the electrode and liquid dielectric [36, 37] and the ability of the electrode to inject space charge into the liquid. Thus, the electric-field distribution of the gap between the plates is changed.

The three groups of electrodes before and after surface modification showed bipolar injection in propylene carbonate. The space charge of the electrode materials treated by a magnetron-sputtering plasma was clearly reduced, which indicates that the plasma layer effectively suppressed charge injection. The effects of surface modification on charge injection of the different electrode materials were different. The amount of charge injected per unit time was related to the contact properties of the metal electrode and the liquid interface, the work function of electrode materials, and the field strength at the metal electrode/liquid interface [10]. Owing to the difference of the Fermi energy levels between the electrode materials and liquid dielectrics, electrons transferred at the interface, resulting in bending of the interfacial energy bands and the formation of a double electrode layer [38], and the
The experiment was \(9.3 \times 10^6\) electrons. The distortion of the electric field near the cathode is due to the height for electron and hole injection, impulse insulation characteristics of liquids. According to the existence of space charge, the electric field distorted, providing a higher electron work function. The negative charge injection mainly derives from electron tunnelling of the cathode. The charge injection can be expressed by the equation below:

\[
J = A E^m \exp\left(-\frac{B}{E}\right)
\]

where \(A\) and \(B\) are constants. The average electric field applied in the experiment was \(9.3 \times 10^6\) V/m. Owing to the electric-field distortion near the plate, the electric-field distortion near the local probeuterance of the cathode surface was obvious. Electron tunnelling can occur and because of the existence of the surface layer, the distortion of the electric field near the cathode is reduced such that the space charge injection of the cathode material after surface modification decreased (\(\phi_g\) and \(\phi_h\) are the barrier heights for electron and hole injection, \(E_F\) is Fermi energy level, \(\phi_m\) and \(\phi_d\) are the work functions of the electrode metal and insulator, \(\chi\) is the electron affinity of the insulator, \(I\) is the ionisation potential energy of the insulator, \(E_g\) is the forbidden bandwidth, \(E_C\) and \(E_V\) is the bottom of the conduction band, and \(E_V\) is the top of valence band.).

After surface modification of the aluminum, copper, and stainless-steel electrodes, the breakdown voltage of propylene carbonate increased by 7, 4, and 9%, respectively. Owing to the existence of space charge, the electric field distorted, providing a seed charge for the development of streamers, which degraded the impulse insulation characteristics of liquids. According to the above analysis, three groups of electrodes showed a bipolar charge injection. The space charge injection decreased after surface modification of the electrodes. Thus, the seed charge for streamer development decreased. Thereby, the impulse breakdown voltage of propylene carbonate improved.

Conversely, the discharge of liquid started from the electrode and then passes through the gap, whereas electric-field distortion weakened the electric field at the interface of the electrode. The electric field of the stainless-steel electrode near the electrode plate was the lowest and the initial stage of streaming was inhibited (Figs. 11 and 12). Therefore, the breakdown voltage of propylene carbonate was the highest before and after modification of the stainless-steel electrode.

5 Conclusions

A low-temperature plasma produced by magnetron sputtering was used to modify the surface of three types of electrode materials, namely aluminium, copper, and stainless steel. We measured the surface morphology changes before and after surface modification, and the impulse breakdown and space charge of propylene carbonate. The charge injection and impulse of the liquid dielectric after sputtering TiO\(_2\) on the surface of the electrode were studied. Our results show that the impulse breakdown voltage of propylene carbonate increases by 7, 4, and 9% after sputtering TiO\(_2\) on the surface of the aluminium, copper, and stainless-steel electrodes, respectively. Surface morphology analyses show that the surface roughness of the electrode is reduced by sputtering TiO\(_2\), which decreases the electric-field distortion of propylene carbonate and the space charge to varying degrees. The injection of space charge is also inhibited. We attribute these results to the following reasons: electrons strike the electrode produced during sputtering changes to the microstructure of the electrode surface, increasing the solid–liquid contact barrier, inhibiting the charge injection of the anode and reducing the seed charge of the streamer development; hence, the impulse breakdown voltage of propylene carbonate increases. Second, deposition of sputtered TiO\(_2\) films on the electrode surface increases the surface shielding layer and weakens the electric-field distortion, which reduces electron tunnelling of the cathode. Thus, a low-temperature plasma produced by magnetron sputtering modifies the surface of the electrode, and affects the space charge injected into the liquid dielectrics, leading to an improvement in the breakdown performance of the liquid. Thus, we have extended the application of plasma modification technology.

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7 References

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