Influence of the Semiconductive Composites Doped with Li4Ti5O12 on Space Charge Implantation in LDPE

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Research Article

Keywords: Li4Ti5O12 nanopowder, semiconductive composites, space charge injection, positive temperature coefficient effect

DOI: https://doi.org/10.21203/rs.3.rs-263584/v1

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Abstract

Space charge accumulation in the insulating layers of high-voltage directed current (HVDC) cables is the key factor that leads to their degradation and limits the operation safety. Hence, it is necessary to effectively inhibit carrier implantation to these layers. In this study, a new method is proposed to suppress the charge implantation to the cable insulation layer, a certain amount of Li$_4$Ti$_5$O$_{12}$ nanopowder is doped in the semiconductive screen to enhance the internal conductive network and homogenize the electric field. The influences of Li$_4$Ti$_5$O$_{12}$ particles in the semiconductive composite screen on the positive temperature coefficient effect and space charge injection process are explored. The obtained results reveal that the charge quantity in the insulation layer corresponding to the minimum peak resistivity is reduced by 49.7%, 58.9%, and 46.9% after the polarization at a Li$_4$Ti$_5$O$_{12}$ content of 4 wt.% and electric field strengths of 10, 20, and 30 kV/mm, respectively.

1 Introduction

High-voltage direct current (HVDC) transmission systems have many practical applications owing to their advantages, including low line costs, large long-distance transmission capabilities, and the ability to transmit high power underground or underwater [1–4]. However, operation safety is compromised by two issues that must be urgently resolved. The first issue is the space charge accumulation in the insulating material that leads to numerous problems such as degradation and aging, partial discharge, and premature insulating failure [5–8]. The second issue is a positive temperature coefficient (PTC) effect that is always observed for semiconductive nanocomposites. This effect increases the resistivity of a semiconductive compound with an increase in temperature. When the temperature reaches a critical value, it increases drastically, leading to a local overheating of the semiconductive screen, which deteriorates its ability to suppress charge implantation [9, 10]. Hence, the development of safe HVDC cables requires mitigating the PTC effect and inhibiting space charge implantation to the insulating layer [11–13].

The idea of minimizing space charges in the insulation layer has attracted considerable attention in the past decades. For its realization, researches focused on the mechanisms of the charge injection and charge trapping processes; as a result, several methods for suppressing space charge accumulation, including the addition of certain types of nanoparticles to the insulation material, were developed [14–17]. However, few studies have investigated semiconductive screen layers, although they play a critical role in homogenizing the high electric field and inhibiting charge implantation to the insulating layer. Usually, a semiconductive screen consists of two layers in a single core HVDC cables: an inner layer sandwiched between the copper conductor and the insulating layer and an outer layer sandwiched between the insulating layer and the wire metallic shield. Furthermore, doping a screen material with ionic conductors such as La$_{0.8}$Sr$_{0.2}$MnO$_3$, La$_{0.6}$Sr$_{0.4}$CoO$_3$, or SrFe$_{12}$O$_{19}$ magnetic particles represents an effective way of enhancing the conductive network and inhibiting space charge implantation [18–20]. A typical semiconductive screen is fabricated from a composite material consisting of a polymeric matrix,
low-density polyethylene (LDPE), ethylene-vinyl acetate copolymer (EVA), and carbon black (CB) particles [21–24], which are dispersed across the matrix to form a conductive network.

The ionic conductor Li$_4$Ti$_5$O$_{12}$ (LTO) with a spinel structure has been examined by various researchers as a promising electrode material [25, 26]. It possesses characteristic properties, including small structural changes during charge–discharge cycles. In particular, the insertion of Li$^+$ ions into the Li$_4$Ti$_5$O$_{12}$ lattice or their extraction from this lattice causes minor changes in the lattice dimensions; therefore, Li$_4$Ti$_5$O$_{12}$ is called “a zero-strain insertion compound.” Note that Li$_4$Ti$_5$O$_{12}$ has a high Li$^+$ diffusion coefficient [27, 28].

The objective of this study was to investigate the inhibition of the PTC effect and carrier transport to the insulating layer by a Li$_4$Ti$_5$O$_{12}$ semiconductive shielding layer. For this purpose, a small amount of Li$_4$Ti$_5$O$_{12}$ and 25% CB serving as a co-doping conductive filler were blended with appropriate amounts of LDPE and EVA by a melt blending method, and the morphology of nanoparticles and microstructures of the produced nanocomposites were examined. Material resistivities at different temperatures were measured to evaluate the PTC effect of these nanocomposites, while the thermal stimulation depolarization current (TSDC) test and pulse electro-acoustic (PEA) measurements were performed to characterize their inhibitory effects on the carrier transport to the insulation layer.

## 2 Materials And Methods

### 2.1 Materials

Lithium acetate (C$_2$H$_3$LiO$_2$), tetrabutyl titanate (TBT) [Ti(OC$_4$H$_9$)$_4$], and acetic acid (C$_2$H$_4$O$_2$) were obtained from Aladdin Co. Ltd. (Shanghai China). Anhydrous ethanol was purchased from Sinopharm Chemical Co. Ltd. (Shanghai, China). These reagents were of analytical reagent grade. LDPE (Kunlun 18D) was purchased from National Petroleum Corporation (Daqing, Heilongjiang, China). EVA copolymer (EVA 7470) was purchased from Formosa Plastics Co. Ltd. (Taiwan China), and conductive CB (VXC-72) was obtained from Cabot Co. Ltd. (Boston, MA, US).

### 2.2 Synthesis of Li$_4$Ti$_5$O$_{12}$ nanopowder

To prepare an ionic conductor with uniform morphology, narrow particle size distribution, and high homogeneity, a sol-gel technique was used to synthesize a Li$_4$Ti$_5$O$_{12}$ precursor, which was subsequently sintered to obtain Li$_4$Ti$_5$O$_{12}$ compound with a spinel structure. An appropriate amount of anhydrous lithium acetate and TBT were weighed at a Li$^+$: Ti$^{4+}$ molar ratio of 0.82:1. Anhydrous lithium acetate was dissolved in a mixture composed of anhydrous ethanol, acetic acid, and deionized water (V: V: V = 120: 10: 5) at a molar ratio of 1:50 (Liquid A). TBT was dissolved in anhydrous ethanol at a molar ratio of 1:60 (Liquid B). Liquid B was placed into an oil bath at 55°C and subjected to vigorous stirring. Liquid A was gradually dropped into liquid B to produce a colorless and transparent solution. To obtain a stable colloidal solution, the reaction solution was aged for 4 h at 55°C under vigorous stirring. The resulting gel was heated to 80°C to extract excess anhydrous ethanol, water, and an organic precursor. Next, the
organic precursor was dried at 150°C, transferred to a muffle furnace, and carbonized for 4 h at 500°C. After that, the furnace temperature was increased to 800°C, and the sample was sintered for 6 h. As a result, lithium titanate with a spinel structure was obtained [25, 26, 29].

The synthesized Li₄Ti₅O₁₂ was ground in a planetary ball mill (MiQi YXQM-4L) for a certain period (10 hours, 20 hours and 30 hours). According to the ball milling procedure described elsewhere [30], the sample was divided into two equal parts and placed into a pair of nylon cans, followed by the addition of zirconia balls with different sizes at a weight ratio of 1:20 and anhydrous ethanol in the amount corresponding to 75% of the reactor capacity. The rotating speed was set to 300 rpm, and the ball milling time was increased at 10-h intervals until Li₄Ti₅O₁₂ was milled into nanopowder with uniform particle sizes. Samples were taken out every 10 h for structural and morphological analysis by X-ray diffraction (XRD, D-MAX 2500/PC) and field emission scanning electron microscopy (FE-SEM, FEI/Nova Nano SEM 450), respectively, to determine the optimal ball milling time.

2.3 Preparation and characterization of Li₄Ti₅O₁₂ semiconductive composites

Li₄Ti₅O₁₂ semiconductive composites were manufactured in two steps by a melt blending method. Initially, 45wt.% LDPE, 30wt.% EVA, and 25wt.% CB particles were fused together at 150°C with a two-roll miller (HaPro). Next, 1 wt.%, 2 wt.%, 3 wt.%, 4 wt.%, and 5 wt.% of the Li₄Ti₅O₁₂ nanopowder and 2wt.% of the crosslinking agent were blended with the pre-mixed materials for 12 min at 120°C using a mixed torque rheometer (RM-200C, HaPro) to obtain LTO semiconductive materials. Simultaneously, the premixed product was blended without Li₄Ti₅O₁₂ during the first step under the same conditions. The produced nanocomposites with different Li₄Ti₅O₁₂ contents were shaped into sheets with various sizes for different electric performance analyses using a hot press apparatus (SKZ401) as follows. First, a nanocomposite was placed in a flat vulcanizer at a temperature of 130°C no pressure for 4 min and then under a pressure of 10 MPa for 6 min. In the next step, a cross-linking reaction was performed at a pressure of 10 MPa and temperature of 180°C for 15 min. Finally, the specimen was cooled for 10 min under a pressure of 10 MPa.

To obtain the distribution of Li₄Ti₅O₁₂ nanoparticles in the composite matrix, the microstructures of the LTO semiconductive composites with Li₄Ti₅O₁₂ contents of 1 wt.%, 4 wt.%, and 5 wt.% were observed by FE-SEM and HRTEM (FEI·Tecnai·G2F30) after being sliced in liquid nitrogen, and their elemental energy dispersive spectroscopy (EDS) analyses were performed.

2.4 Resistivity measurements

Because the thermal expansion coefficient of the polymer is three times larger than that of CB particles, the polymer matrix expands with increasing temperature. As a result, the CB particles become diluted, inhibiting their charge transfer and leading to the blockage of conductive channels, which increases the
resistivity of the nano-compound [31, 32]. Hence, resistivity represents an important characteristic of the conductive channels inside semiconductive composites.

The specimen for resistivity testing was a sheet with a length of 110 mm, width of 50 mm, and thickness of 0.5 mm. Its resistivity was measured at temperatures of 30, 40, 50, 60, 70, 80, 90, 100, and 110°C using a semiconductive rubber and plastic material resistivity tester (DB-4). The specified temperature range corresponds to the operational conditions of the HVDC cable.

2.5 TSDC testing

TSDC can accurately reflect the space charge amount in an insulating material; thus, TSDC measurements represent a widely used technique for studying the parameters of space charges in the insulation layer [33]. To examine the influence of Li$_4$Ti$_5$O$_{12}$ concentration on the suppression of carrier transport under the action of a powerful electric field, the TSDC generated in the insulation was determined. For this purpose, the insulating layer was polarized by high voltage under the shield of a LTO semiconductive nanocomposites. The utilized polarization device included a high negative voltage DC source, a couple of copper cylindrical electrodes with diameters of 25 mm. The LTO semiconductive layer was placed between the cathode and the insulating sheet used as the shelter, and a plastic shielding box used for screening (Fig. 1). The thickness of the LTO semiconductive layer was 0.5 mm. The insulating layer is an LDPE film with a thickness of 0.3 mm and uniform structure. The surfaces of the insulating and semiconductive layers were cleaned with anhydrous ethanol and dried for 4 h at 60°C before testing. The polarizing electric field strength was varied between 10, 20, and 30 kV/mm, and the polarization time was 30 min.

After the polarization process was complete, the LDPE depolarization current was measured using a Novocontrol Concept-80 wide band dielectric spectrometer. The starting temperature was 20°C, the heating rate was 3°C/min, and the final temperature was 90°C.

2.6 Space charge distribution measurements

The space charges in the insulation layer can be classified into two types: homo-charges originated from the electrode (metal core) emission, and hetero-charges caused by the material impurities ionized under high stress [34]. When the electric field strength is sufficientely high (for example, 10 kV/mm or more), the implanted charges from the core become predominant, which is the major reason for the space charge accumulation in the insulation layer.

To investigate the inhibitory effect of the produced LTO semiconductive composites on the space charge implantation to the insulating material, PEA measurements were performed. During the test, an LTO semiconductive sheet was placed between the cathode and the insulating layer not only for acoustic impedance matching but also for suppressing the simultaneous charge injection into the insulation layer [35]. In this process, a high voltage was applied through the upper electrode to simulate charge injection, and a high-voltage electric pulse was applied at the same time to cause a small displacement of the charge in the insulating sheet. This slight movement was transferred to the piezoelectric sensor as a
sound wave that was subsequently detected and transmitted to a computer for analysis. Thus, the distribution of space charges in the insulating layer was represented by the obtained charge density. A schematic of the utilized PEA measurement setup is shown in Fig. 2.

In this test, the influence of Li$_4$Ti$_5$O$_{12}$ content in the semiconductive composites on the space charge distribution was explored, and an LDPE layer with a thickness of 0.3 mm was used as the insulation medium. The test electric field strength was varied between 10, 20, and 30 kV/mm, and the applied voltage was maintained for 30 min.

3 Results And Discussion

3.1 Characterization

3.1.1 Characterization of Li$_4$Ti$_5$O$_{12}$

The XRD patterns of the Li$_4$Ti$_5$O$_{12}$ powder ball-milled for 0, 10, 20, and 30 h are presented in Fig. 3. All patterns are consistent with JCPDS No. 49–0207 exhibiting the characteristic peaks of the spinel Li$_4$Ti$_5$O$_{12}$ structure at 2$\theta$ = 18.3°, 35.6°, 43.2°, 47.4°, 57.2°, 62.8°, 66.1°, and 79.3°, which correspond to the (111), (311), (400), (331), (333), (440), (531), and (444) planes, respectively. Note that the XRD patterns contain no impurity peaks, indicating that the Li$_4$Ti$_5$O$_{12}$ synthesis conditions were optimal. Figure 1 also shows that as the milling time increases, the intensities of the diffraction peaks decrease, which suggests a decrease in the degree of Li$_4$Ti$_5$O$_{12}$ crystallinity due to the ball milling effect. Therefore, the ball milling time of Li$_4$Ti$_5$O$_{12}$ should be as short as possible.

Figure 4 displays the FE-SEM images of the Li$_4$Ti$_5$O$_{12}$ nanopowders fabricated at different ball milling times. As shown in Fig. 4a, most of the untreated Li$_4$Ti$_5$O$_{12}$ particles are clustered together, and several large grain aggregates are present in the sample that was ball-milled for 10 h (Fig. 4b). After ball milling for 20 h, the particle size becomes more uniform, ranging between 300 and 500 nm, and all particle aggregates disappear (Fig. 4c). A comparison of the images presented in Fig. 4c and d reveals that the morphology of the sample ball-milled for 30 h is not significantly different from that of the sample ball-milled for 20 h. Because ball milling considerably decreases the crystallinity of the sample, the optimal ball milling conditions for Li$_4$Ti$_5$O$_{12}$ correspond to a speed of 300 rpm and treatment time of 20 h.

3.1.2 Characterization of Li$_4$Ti$_5$O$_{12}$ semiconductive compounds

Figure 5 displays the FE-SEM and EDS images of the nanocomposites cross-sections. As shown in Fig. 3a–c, Li$_4$Ti$_5$O$_{12}$ particles are well-scattered in the polymer matrix at LTO contents of 1 wt.% and 4 wt.%, and their sizes range between 400 and 800 nm. Figure 3c also shows that Li$_4$Ti$_5$O$_{12}$ particles become larger and agglomerate at high LTO contents. Figure 5d displays the EDS spectrum of the
specimen with a Li$_4$Ti$_5$O$_{12}$ content of 4 wt.%. It shows that the carbon amount is the highest, followed by oxygen and titanium. Hence, the white particles in Fig. 5a–c correspond to Li$_4$Ti$_5$O$_{12}$ particles.

Figure 6 shows the HRTEM images of the nanocomposites cross-sections with Li$_4$Ti$_5$O$_{12}$ contents of 1 wt.%, 4 wt.%, and 5 wt.%. The particles with the light contrast correspond to CB particles, and the particles with the deep contrast represent Li$_4$Ti$_5$O$_{12}$ particles.

Figure 5 and 6 indicate that Li$_4$Ti$_5$O$_{12}$ grains are well-scattered in the polymer matrix at LTO fractions of 1 wt.% and 4 wt.%, although they are slightly larger than those depicted in Fig. 4c. When the Li$_4$Ti$_5$O$_{12}$ fraction reaches 5 wt.%, some Li$_4$Ti$_5$O$_{12}$ particles begin to agglomerate. The SEM and HRTEM images of the prepared composites confirm that Li$_4$Ti$_5$O$_{12}$ particles can be well mixed with other components by the melt bending method when the Li$_4$Ti$_5$O$_{12}$ concentration does not exceed 4 wt.%, while at larger LTO contents, their agglomeration occurs.

### 3.2 Resistivity of LTO semiconductive composites

Figure 7 describes the influence of Li$_4$Ti$_5$O$_{12}$ content on the resistivity of the semiconductive composites. As shown in Fig. 7a, the resistivity of the LTO semiconductive sheet increases more slowly than that of the specimen without Li$_4$Ti$_5$O$_{12}$, and the corresponding curve exhibits the slowest ascending trend at a Li$_4$Ti$_5$O$_{12}$ content of 4 wt.%. As the Li$_4$Ti$_5$O$_{12}$ content increases from 0 to 5 wt.%, the peak resistivity of the LTO semiconductive composite first decreases and then increases. Its minimum of only 116 $\Omega \cdot$cm achieved at a Li$_4$Ti$_5$O$_{12}$ content of 4 wt.% is smaller than that of the specimen without Li$_4$Ti$_5$O$_{12}$ by 48.4% (Fig. 7b), which indicates that the nanocomposites containing 4 wt.% Li$_4$Ti$_5$O$_{12}$ has the optimum conductive network that efficiently suppresses the PTC effect. This is due to the increase in the ionic conductance of Li$_4$Ti$_5$O$_{12}$, which compensates for the decrease in the electronic conductance of CB particles and fracture of the conductive channels caused by their dilution.

According to the results of previous studies [10, 31], crystalline and amorphous phases coexist in polymers, and the majority of ionic conductors can merely disperse at their interface at room temperature. Owing to the large molecular weight difference between inorganic compounds and polymers, the molarity of inorganic particles is much higher than that of polymers. Therefore, if the concentration of ionic grains is high enough and these inorganic grains can be scattered across the matrix, they may collide with each other through thermal motion and thus exchange and transfer charges to form conductive channels that lower the composite resistivity. When the temperature is below the melting point of the polymer, its macromolecular chains cannot move freely, and the three composite phases remain relatively stable; as a result, the composite resistivity increases. When the composite is heated to the polymer melting point, the polymeric phase begins to melt while stretching macromolecular chains, which expands the polymer matrix and dilutes the conductive particles. If the conductive filler contains only CB particles, its conductance would decrease with increasing temperature, accompanied by the partial rupture of the conductive channel caused by CB dilution, which leads to a resistivity increase [31, 32, 36].
Representative diagrams of the charge delivery networks of the prepared semiconductive composites are presented in Fig. 8. Figure 8a depicts the charge transport network formed only by the CB particles in the polymer matrix at room temperature. As the temperature increases, the polymers start to inflate, and the distance between CB particles gradually increases, leading to a decrease in the number of conductive channels. As the temperature rises continuously, an increasingly large number of CB particles become isolated and much more conductive network fracture. In this case, charge delivery becomes more difficult, causing the PTC effect (Fig. 8b). According to the results of previous studies, not only the migration of Li\(^+\) ions, but also the empty d-orbits of Ti\(^{4+}\) ions contribute to the electron transfer process [27, 28]. This facilitates the creation of a stronger conductive network inside the nanocomposites structure after the addition and scattering of Li\(_4\)Ti\(_5\)O\(_{12}\) particles. It is well known that ionic conductivity increases with an increase in temperature, which compensates for the decreased electronic conductivity of CB particles. According to the obtained results, the specimen containing 4 wt.% Li\(_4\)Ti\(_5\)O\(_{12}\) has the lowest peak resistivity near the melting point, which indicates that the ionic conductivity of Li\(_4\)Ti\(_5\)O\(_{12}\) and the electronic conductivity of CB complement each other and that an optimal conductive network is constructed, as shown in Fig. 8c. However, the PTC effect becomes strong again when the Li\(_4\)Ti\(_5\)O\(_{12}\) concentration exceeds 4 wt.%. As reported in previous studies, the majority of inorganic compounds can exist only at the interface between the crystalline phase and the amorphous phase of polymers [9, 36], which limits the space for conductive particles. As a result, excessive Li\(_4\)Ti\(_5\)O\(_{12}\) nanoparticles begin to agglomerate and form oversized grains, as shown in Figs. 5c and 6c. This destroys the conductive network and enhances the PTC effect (Fig. 8d).

3.3 TSDC testing

Figure 9 illustrates the influence of the Li\(_4\)Ti\(_5\)O\(_{12}\) content in a semiconductive material on the thermally stimulated depolarization current in the insulating material after injection. Figures 9a–c show the thermally stimulated depolarization currents shielded by semiconductive sheets containing different Li\(_4\)Ti\(_5\)O\(_{12}\) amounts. Different curve shapes correspond to different Li\(_4\)Ti\(_5\)O\(_{12}\) concentrations in the semiconductive sheets. When the sheet contains 4 wt.% Li\(_4\)Ti\(_5\)O\(_{12}\), the smallest peak current of 3.8×10\(^{-12}\) A is obtained at an electric field strength of 10 kV/mm. Its value is reduced to 2.9×10\(^{-12}\) A at 20 kV/mm and to 2.60×10\(^{-12}\) A at 30 kV/mm, corresponding to relative decreases of 44%, 37%, and 42%, respectively. Figure 9d shows the relationship between the charge quantity in the insulation material and the Li\(_4\)Ti\(_5\)O\(_{12}\) concentration in the semiconductive compound (charge quantities in this work were calculated by integrating the depolarization current curves depicted in Fig. 9a–c). Its value first decreases with an increase in Li\(_4\)Ti\(_5\)O\(_{12}\) concentration and then increases as the latter exceeds 4 wt.%. The minimum charge quantity at electric field strength of 10 kV/mm equals 5.33×10\(^{-9}\) C; its magnitude is further decreased to 3.11×10\(^{-9}\) C at 20 kV/mm and to 3.04×10\(^{-9}\) C at 30 kV/mm, which correspond to relative decreases of 49.7%, 58%, and 46.9%, respectively. Thus, the produced semiconductive composites inhibit space charge implantation most effectively at a Li\(_4\)Ti\(_5\)O\(_{12}\) content of 4 wt.%.
Figure 9 also shows that the depolarization current decreases when the polarizing stress increases from 10 kV/mm to 20 or 30 kV/mm, which is accompanied by the reduction in the charge quantity. These results suggest that the screening effect of the LTO semiconductive composites is enhanced under higher stress because the stress promotes the polarization of Li$_4$Ti$_5$O$_{12}$ molecules. Correspondingly, the electronic cloud of Li$_4$Ti$_5$O$_{12}$ becomes more distorted to generate an electric field that partially offsets the applied electric field. Hence, the movement of space charges is inhibited by the induced electric field generated by the polarized Li$_4$Ti$_5$O$_{12}$ particles as they pass through the semiconductive layer. Moreover, a fraction of these charges cannot pass through the interfacial barrier between the semiconductive layer and the insulating layer due to energy losses. As a result, the space charge amount in the insulating layer is decreased more efficiently at an electric field strength of 20 or 30 kV/mm, indicating that the prepared LTO semiconductive composites can be potentially used in HVDC cables operated at 20–30 kV/mm.

As the Li$_4$Ti$_5$O$_{12}$ content exceeds 4 wt.%, the charge quantity in the insulation layer increases again, which implies that the screening ability of the LTO semiconductive compound is weakened due to the agglomeration of Li$_4$Ti$_5$O$_{12}$ particles, which is confirmed by the corresponding SEM and HRTEM images. Hence, it can be concluded that the optimal Li$_4$Ti$_5$O$_{12}$ concentration is equal to 4 wt.%. 

### 3.4 Space charge distribution

Figure 10 displays the distributions of space charges in the insulating materials polarized at 10, 20, and 30 kV/mm, respectively, and screened with the semiconductive composites containing different Li$_4$Ti$_5$O$_{12}$ amounts (in these experiments, the polarization time was 1800 s). The LDPE sheet with a thickness of 300 µm was selected as the insulation material; thus, the values of zero and 300 µm on the x-axes represent the coordinates of the insulation interfaces. When the same electric field is applied, the amounts of induced charges at the interfaces are almost the same. Hence, the observed differences in the charge distributions originate from charge implantation. Figures. 10a–c show that the interfacial charge density is the smallest when the screening layer contains 4 wt.% Li$_4$Ti$_5$O$_{12}$, and that the charge density in the middle of the insulation layer is close to zero. However, when the screening layer contains 5 wt.% Li$_4$Ti$_5$O$_{12}$, the charge densities at the interfaces and inside the insulating sheets apparently increase, which confirms that space charge accumulation can be effectively inhibited by the semiconductive layer containing 4 wt.% LTO, and that the inhibitory ability of charge injection is weakened when the Li$_4$Ti$_5$O$_{12}$ content exceeds 4 wt.%.

Space charge transport mechanism in semicomposites is complex. Charges emitted by the conductive core are strongly affected by the external electric field ($E_{ex}$) generated by the cable and the induced electric field ($E_{in}$) generated by the distorted electronic cloud of polarized Li$_4$Ti$_5$O$_{12}$ molecules. When semiconductive composites without Li$_4$Ti$_5$O$_{12}$ are used, the electrons emitted by the conductive core pass through the interfacial barrier and move to the insulation layer. Under the action of $E_{ex}$, the force on the charges is only $F_1$, and their tracks are approximately straight, as illustrated in Fig. 11a. When the Li$_4$Ti$_5$O$_{12}$ concentration does not exceed 4 wt.%, particles can be well dispersed in the matrix. As
Li$_4$Ti$_5$O$_{12}$ nanoparticles are polarized by $E_{\text{ex}}$, the electronic cloud becomes deformed and generates an induced electric field $E_{\text{in}}$, the direction of which is opposite to that of $E_{\text{ex}}$. As a result, $F_1$ becomes weakened. According to the rules of electron arrangements outside the nuclei, Ti$^{4+}$ ions have the tendency to attract free electrons to fill their empty orbitals, which implies that Li$_4$Ti$_5$O$_{12}$ particles can attract the moving charges and influence the charge movement via the Coulombic force $F_2$. Meanwhile, the moving charges are affected not only by $F_1$ but also by $F_2$ when they enter the LTO semiconductive composites. Figure 11b presents the results of force analysis of the moving charges in the LTO semiconductive composites, indicating that charge implantation is inhibited by $F_2$.

It is now established that Li$_4$Ti$_5$O$_{12}$ particles agglomerate at Li$_4$Ti$_5$O$_{12}$ contents above 4 wt.%, which reduces the effective concentration of Li$_4$Ti$_5$O$_{12}$ and weakens the $E_{\text{in}}$ field. Furthermore, the oversized grains increase the interface roughness, which will distort the interfacial electric field. This changes the force on the moving charges, increases $F_1$, and decreases $F_2$, as shown in Fig. 11c.

In summary, the force on the moving charges in the semiconductive screen is strongly related to the Li$_4$Ti$_5$O$_{12}$ concentration. When the Li$_4$Ti$_5$O$_{12}$ content exceeds 4 wt.%, the inhibitory effect of the LTO semiconductive composites on charge injection is weakened and can be even reversed, as indicated by the results of the PEA and TSDC tests. The obtained PEA curves show that the charge densities near the interfaces apparently increase when shielded by the specimen containing 5 wt.% Li$_4$Ti$_5$O$_{12}$ (the same trend is observed for the TSDC curve peaks). Moreover, both the decrease in the effective concentration of Li$_4$Ti$_5$O$_{12}$ particles and distortion of the interfacial electric field promote charge accumulation.

4 Conclusions

The results of this study suggest that the addition of a certain amount of ionic conductor Li$_4$Ti$_5$O$_{12}$ can enhance the composites conductive network, mitigate the electric field distortion, and effectively weaken the space charge injection into the insulating layer. Its main conclusions are summarized as follows:

When the Li$_4$Ti$_5$O$_{12}$ content is 4 wt.%, both the PTC effect and charge implantation process are significantly inhibited. The peak resistivity of the obtained composite was 48.4% lower than that of the sample without Li$_4$Ti$_5$O$_{12}$. Simultaneously, the minimum charge amount in the insulation layer was reduced by 49.7% at an electric field strength of 10 kV, by 58.9% at 20 kV/mm, and by 46.9% at 30 kV/mm. Moreover, the minimum peaks of the depolarization currents obtained at 10, 20, and 30 kV/mm were reduced by 44%, 37%, and 42%, respectively. Because the space charge transport is strongly influenced by the external electric field, the induced electric field and Coulombic force on the polarized Li$_4$Ti$_5$O$_{12}$ particles can counteract a fraction of the external electric field. The horizontal component of the Coulombic force may also prevent charge migration to the insulating layer, and the vertical component of the Coulomb force deflects the charge migration direction in the LTO semiconductive composites. Thus, a considerable number of charges become blocked at the interface between the semiconductive and insulating layers.
When the Li$_4$Ti$_5$O$_{12}$ concentration reaches 5 wt.%, the PTC effect becomes more pronounced (as compared with that of the sample containing 4 wt.% Li$_4$Ti$_5$O$_{12}$), and the charge accumulation process is facilitated by the agglomeration of Li$_4$Ti$_5$O$_{12}$ particles. This decreases the effective concentration of Li$_4$Ti$_5$O$_{12}$ particles and increases the interfacial roughness of the nanocomposites, which in turn promotes the electric field distortion and charge implantation processes. Therefore, the findings of this work may help develop novel and efficient semiconductive screening materials for HVDC cables.

**Declarations**

**Acknowledgements**

This research study was financially supported by the State Grid Shandong Electric Power Research Institute (grant No. SGSDDK00KJJS1900329).

**Conflicts of interest**

The authors declare that they have no conflict of interest.

**Authors’ contributions**

Hongxia Yin: methodology, Investigation, data curation, writing-original draft, review and editing, project administration. Shiyi Zhao: Investigation. Chuncheng Hao: resources, funding acquisition, Qingquan Lei: conceptualization.

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