Study on the Electrochromic Label for High-voltage Equipment with Wo₃

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Abstract. Whether the equipment is charged or not is a working procedure that must be carried out to ensure the safety of personnel during the power failure maintenance work on the power transmission and transformation equipment. At present, UHV power transmission equipment mainly uses contact, non-contact electroscope to check whether the equipment is electrified. However, this type of electroscope needs a wide response range because the stray capacitance to ground is greatly affected by the actual working environment and operating position. At the same time, the contact type high voltage electroscope generally needs to be used with the insulated test pole. As the voltage level rises, the required safety distance increases. The length and deflection of the test pole cannot meet the requirements. The overall quality is larger and the operation is inconvenient. The use of material colour changes to indicate the charged state of the device is a promising technical means. Based on the electrochromic technology, this paper makes use of tungsten trioxide materials to prepare charged state indicator materials for UHV transmission equipment, and characterizes whether the equipment is charged by the colour change of materials. Experiments show the effectiveness of the material.

1. Introduction
Before carrying out related operations on some power outages, it is necessary to conduct the power test first to verify that there is no voltage on the electrical equipment or transmission lines, to prevent the occurrence accidents such as charged ground wire or contacting with charged equipment. At present, UHV power transmission equipment mainly uses contact, non-contact electroscope for charged state detection [1]-[2]. Contact electroscope cannot effectively solve the problem of detecting the live state of DC equipment [3]-[4]. Non-contact electroscope can detect the electric function by detecting the electric field or partial discharge in the vicinity of the charged equipment, but it has the advantages of accuracy, adaptability, cost performance, etc. insufficient. And, in the UHV substation, converter stations and other electromagnetic environment complex places, the reliability of non-contact electroscope is poor [5]. It is of great practical significance to develop new technical means to detect the charged state of equipment.

Inorganic electrochromic materials have become an increasingly active research field, and gradually applied to new energy-saving windows, building glass curtain walls, large passenger aircraft and other fields [6]. In this paper, electrochromic materials are applied to the power system to indicate the charged state through the change of material colour.

2. Electrochromic mechanisms
Electrochromism refers to the reversible change of the material between the colored state of low transmissivity or the decolorized state of high transmissivity by the injection or extraction of charges (ions or electrons) by the action of alternating electric fields [7]. Appearance performance is reflected in the reversible changes in colour and transparency. Depending on the internal characteristics of the
different electrochromic materials and their combination, they can produce a great deal of transmittance and reflectivity regulation in the visible and solar spectrum, even in the microwave range.

Since the discovery of the electrochromism of WO₃ thin films by Deb in 1969 [8], extensive research has been carried out on inorganic materials, and great progress has been made. Inorganic electrochromic materials are mostly transition metal oxides or hydroxides, such as WO₃, MoO₃, TiO₂, V₂O₅, Ni (OH)₂ and the like. WO₃ has the characteristics of high colour contrast; good cycle stability and good thermal stability, making tungsten trioxide become the most studied and commercially available inorganic material in recent years [9].

Ideally, crystalline WO₃ can be considered as a deformed perovskite-type crystal structure. As shown in Fig 1(a), the chemical bond is an ionic bond between W⁶⁺ and O²⁻, but also has obvious covalent components. This distorted perovskite structure consists of the [WO₆] octahedron with octahedral stacking. Tungsten atoms are located in the center of the octahedron and each oxygen atom is shared by two [WO₆] octahedrons as bridging oxygen. Among WO₃ crystal phases, the hexagonal WO₃ lattice has one-dimensional ion channels in the lattice, which is conducive to ion transport and diffusion. Crystal water in the hydrated WO₃ lattice also enhances ion transport efficiency. Therefore, its electrochromic properties are also relatively good. In addition, there are a variety of metallic non-stoichiometric phase in the tungsten oxide material system, as shown in Fig 1(b), often with excellent optoelectronic properties.

(a) tungsten oxide non-stoichiometric structure diagrams

Figure 1 tungsten oxide structure (a) non-stoichiometric structure, (b) ideal tungsten oxide structure
Oxygen vacancies are often present in tungsten oxide and combine with the electrons injected into the cathode to form a colour center when voltage is applied, thereby inducing electrochromism [10]. The specific mechanism can be expressed by the following (1) and (2):

\[
V_{o}^{+} + e^{-} \leftrightarrow [V_{o}^{+} + e^{-} ] \quad (1)
\]

\[
V_{o}^{2+} + 2e^{-} \leftrightarrow [V_{o}^{2+} + 2e^{-} ] \quad (2)
\]

3. Preparation of electrochromic materials

The WO₃ sol and the MoO₃ sol are first prepared, and then the two are mixed and treated with a stabilizer. Table 1 shows the reagents and related drugs used in the experiment. The drugs used are of analytical grade, including tungsten powder and molybdenum powder are 200 mesh sizes.

| Name                              | Structural formula | Level and purity | Manufacturer or supplier   |
|-----------------------------------|--------------------|------------------|----------------------------|
| Metallic tungsten powder          | W                  | A.R>99.8%        | Tianjin Reagent Co.        |
| Metallic molybdenum powder        | Mo                 | A.R>99%          | Shanghai Reagent Co.       |
| Hydrogen peroxide                 | H₂O₂               | A.R>30%          | Tianjin Reagent Co.        |
| Anhydrous ethanol                 | C₂H₅OH             | A.R>99%          | Hengyang Reagent Co.       |
| Glacial acetic acid               | HAc                | A.R>99%          | Changsha Reagent Co.       |

![Figure 2. Preparation WO₃-MoO₃ hybrid sol](image-url)
The preparation of WO$_3$ sol process is briefly described as follows:

- A certain amount of W powder was weighed with an analytical balance into a round bottom flask, excess H$_2$O$_2$ (30 vol% concentration) was added dropwise and magnetically stirred in an ice-water bath for 24 hours;
- With platinum black mesh catalytic decomposition of excess H$_2$O$_2$, filtered to give a light yellow transparent sol;
- Then, an appropriate amount of C$_2$H$_5$OH and HAc were added to the sol as a stabilizer to prepare WO$_3$ sol.
- The preparation of MoO$_3$ sol is the same as WO$_3$.

The prepared WO$_3$ sol and MoO$_3$ sol are mixed according to a certain proportion, and the magnetic stirring WO$_3$-MoO$_3$ mixed sol is obtained after the magnetic stirring for 1 hour. The technological process is shown in Fig 2.

The prepared sol is shown in Fig 3. The low concentration of sol is a pale yellow clear solution, although it’s clear but tending phenomenon can be observed, which indicates the presence of colloidal cluster particles. High concentrations of tungsten oxide pigment particle dispersion is completely opaque, showing a dark yellow sticky state, but still remain at room temperature for more than a month without significant precipitation, indicating sufficient stability of the pigment particle dispersion.

![Figure 3. The prepared sol.](image)

![Figure 4. The WO$_3$ coating material.](image)

Sol gels usually require the addition of stabilizers, also known as dry-control chemicals (DCCA), which are a class of organic liquids with a low vapour pressure. They can stabilize the particle size of the gel network and the size of the network gap, allow uniform distribution of tension in the gel without cracking, and shorten of the drying cycle. Select glycerol as a drying control agent, and control the amount added about 2%. The prepared WO$_3$ coating material is shown in Fig 4.

4. Performance Testing

Wipe clean the hollow steel pipe, and then apply the WO$_3$ coating to the steel pipe, and apply a coating thickness of 1mm and 2mm on each steel pipe respectively. The length of each coating is about 10cm. The paint then dries naturally, as shown in Fig 5.

![Figure 5. Steel pipes coated with WO$_3$. (a) thick coating; (b) thin coating.](image)

Connected the hollow pipe to the regulator, and then applied 500mA current to the pipe for 30 minutes. Material remains yellow and no colour change appears. Then, we increased the current to 200A, and the material started to change colour slowly. Thirty minutes later, the colour of the material is as shown in Fig 6.
The experimental results show that when the current of 500mA passed to the steel pipes, no colour change occurred after half an hour of energization, regardless of the thickness of the material. When the hollow steel pipes were connected with a large current of 200A, the materials undergone obvious discoloration phenomenon after half an hour. Most of the paint changed from the original yellow to blue-violet, and the colour change of thinner areas was significantly larger than that of thicker area. After the power is off, the colour of the material gradually resumes within half an hour.

5. Conclusion
This paper attempts to use the colour change of materials to indicate the charging status of high-voltage power transmission equipment. A tungsten oxide-based pigment particle sol was prepared, a stabilizer was added to the dispersion, and a tungsten oxide coating was obtained after sufficiently stirring. Tests show that the paint can be discoloured under the action of high current for a long time, indicating the charged state of the equipment. Although the colour change of the material has a time delay and is not effective for small currents, it is still a meaningful exploration.

6. References
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