Study on Method for Chemical Reaction Activation Energy Acquiring of Dry Insulation Equipment Based on TGA

Xin Zhang\textsuperscript{1,}\textsuperscript{*}, Xinjie Zhang\textsuperscript{2,\textsuperscript{a}}, Hao Ma\textsuperscript{1,\textsuperscript{b}}, En Wang\textsuperscript{3,\textsuperscript{c}}, Wei Wang\textsuperscript{1,\textsuperscript{d}}, Xiaoguang Ma\textsuperscript{1,\textsuperscript{e}} and Chao Dun\textsuperscript{4,\textsuperscript{f}}

\textsuperscript{1}Electric Power Research Institute, State Grid Tianjin Electric Power Corporation, Tianjin, China
\textsuperscript{2}Chengxi Power Supply Branch, State Grid Tianjin Electric Power Corporation, Tianjin, China
\textsuperscript{3}State Grid Tianjin Electric Power Corporation, Tianjin, China
\textsuperscript{4}Maintenance Company, State Grid Tianjin Electric Power Corporation, Tianjin, China

\textsuperscript{*}Corresponding author e-mail: zhangxin_sgcc@126.com, \textsuperscript{9}10877245@qq.com, \textsuperscript{\textsuperscript{a}}910877245@qq.com, \textsuperscript{\textsuperscript{b}}goatma@163.com, \textsuperscript{\textsuperscript{c}}horse_en90@163.com, \textsuperscript{\textsuperscript{d}}qq973641254@163.com, \textsuperscript{\textsuperscript{e}}xiaoguang.ma@tj.sgcc.com.cn, \textsuperscript{\textsuperscript{f}}chao.dun@tj.sgcc.com.cn

Abstract. Thermogravimetric analysis is an important method in chemical reaction kinetic analysis. This paper introduces thermogravimetric analysis into the field of insulation performance analysis of dry insulation equipment, and introduces the thermogravimetric analysis experimental methods of epoxy resin materials. On this basis, the calculation principle of the activation energy of the chemical reaction is analysed, and two calculation methods for the activation energy of dry insulation equipment are proposed.

1. Introduction

Dry-type insulation equipment such as dry-type transformers and dry-type reactors are important electrical equipment in power systems. These are responsible for tasks such as voltage conversion, distribution, and transmission of electrical energy. Their operating status directly affects the safe and stable operation of the entire power grid. Generally, dry insulation equipment has the advantages of good fire resistance, heat resistance and short circuit resistance, safety and environmental protection. However, because the main insulation of dry equipment is cast by epoxy resin, its insulation performance, insulation aging degree and remaining life are difficult to detect and evaluate, which brings hidden dangers to the operation and maintenance of dry equipment. [1-3]

At present, research on the insulation monitoring of dry-type insulation equipment is mainly focused on the detection of macro electrical parameters such as partial discharge and dielectric performance. These methods are not very effective for identifying latent insulation defects and sudden insulation failures, so it is difficult to scientifically evaluate the remaining life of dry equipment. [4, 5]

Activation energy, as a parameter that can measure the easiness of chemical reactions, is of great significance in chemical reactions. By accurately obtaining the activation energy of dry-type insulation equipment, the aging degree of dry-type insulation equipment can be detected from the nature of the
insulating material. This article will start from the Thermogravimetric Analyzer (TGA) of epoxy resin materials, and explore the method for obtaining the chemical reaction activation energy of dry insulation equipment.

2. Thermal weight loss experiment of epoxy resin

2.1. Test sample preparation

Taking dry-type transformers as an example, referring to the dry-type transformer manufacturing process, insulation materials, and main structure in engineering applications, the corresponding scale-down test models and material slices are developed, as shown in Figures 1 (a) and (b), respectively.

![Sample of dry-type transformer](image1)

![Sample of epoxy resin](image2)

Figure 1. Experimental samples.

The scale-down test model can basically achieve the assessment of the manufacturing process and the performance of the transformer insulation equipment; the insulation material slice is mainly used for the test of various physical and chemical properties and electrical properties, and the study of the material aging mechanism.

Epoxy resin material slices can be produced in two ways. One is to directly produce a sample of the epoxy resin sheet of the specified size according to the manufacturing process and materials of the dry-type transformer on the spot; the other is to reduce the size of the transformer model. Use punches, microtome, and other equipment to make wafer-type slice samples.

2.2. Thermal weight loss test process

The main steps of the thermal weight loss experiment of epoxy resin chips are as follows:

1. Grind the epoxy resin material into powder, take a 10mg test sample into a 70ul alumina crucible, and tap the crucible to fully contact the sample.

2. TGA-DSC3+ simultaneous thermal analysis combined test was used. Before the experiment, the outlet pressure of the valve was controlled to 0.1MPa, and high-purity nitrogen was passed in for 30 minutes to exhaust the gas in the furnace.

3. Set the heating rate of 5K/min, 10K/min, 15K/min, 20K/min, 25K/min, increase the temperature in the furnace to 800°C, and record the data of the sample quality as a function of temperature.

4. Repeat the above process to obtain the thermal weight (TG) loss curve and the first-order differential curve (DTG) of multiple sets of epoxy resin samples. Typical TG and DTG curves obtained by TGA are shown in Figure 2.

2.3. Analysis of test results

After analyzing the results of typical thermogravimetric analysis of epoxy resin, the following conclusions can be drawn:

1. The heating rate has a great influence on the TG curve of epoxy resin. As the heating rate increases, the TG curve shifts toward high temperature. The reason for this phenomenon is that the
temperature rise of the sample mainly depends on the heat transfer between the crucible and the sample. The temperature difference between the heated crucible and the sample causes a temperature gradient inside the sample, and the temperature difference effect of the sample follows increasing the heating rate increases.

![TG curve of epoxy resin](image1)

(a) TG curve of epoxy resin  ![First order DTG curve of epoxy resin](image2)

(b) First order DTG curve of epoxy resin

Figure 2. Typical curve of TGA.

(2) As the heating rate increases, the initial decomposition temperature, termination decomposition temperature, and peak temperature of the sample increase correspondingly, but the five thermal weight loss curves of the sample are roughly similar.

(3) The typical thermal weight loss curve has two distinct steps. The mass loss of step I accounts for about 5% of the total mass loss, and the temperature corresponding to the maximum reaction rate is between 210°C and 250°C; the mass loss of step II accounts for about 65% of the total mass loss, and the maximum reaction rate The corresponding temperature is between 360°C and 400°C. These thermal weight loss curves provide a basic basis for calculating the chemical reaction activation energy.

3. Calculation method of chemical reactions activation energy

It is assumed that the reaction process of a substance depends only on the conversion rate \( \alpha \) and the temperature \( T \). These two parameters are independent of each other. The kinetic equation of the reaction at indefinite temperature and heterogeneous phase can be expressed as

\[
\frac{d\alpha}{dt} = f(\alpha)k(T)
\]  

(1)

In the formula, \( t \) is time, \( k(T) \) is a temperature relationship formula of rate constant, and \( f(\alpha) \) is a reaction mechanism function. In linear heating, through the conversion of temperature and time, the above formula can be transformed into the following form.

\[
\frac{d\alpha}{dT} = \frac{1}{\beta} f(\alpha)k(T)
\]  

(2)

\[
\beta = \frac{dT}{dt}
\]  

(3)
\( \beta = dT/dt \) is the heating rate. In most tests, the heating rate is a fixed value. Equation (2) is the most basic equation of reaction kinetics in isothermal and non-isothermal processes. All other equations are derived on the basis of this equation.

Substituting the Arrhenius equation into equation (2), we can obtain the kinetic equations of heterogeneous systems under non-constant temperature conditions.

\[
\frac{d\alpha}{dT} = \left( \frac{A}{\beta} \right) \exp\left( - \frac{E_a}{RT} \right) f(\alpha)
\]  

3.1. Equal conversion rate method

Among various methods of TGA data analysis, the equal conversion rate method has been widely used. Its main principle is: for the same kind of reaction of the same substance, perform experiments at different heating rates, such as \( \beta_1, \beta_2, \ldots \), and finally get a set of curves about \( \alpha \) and \( T \). Select an \( \alpha \) in the DTG curve figure and use it as a horizontal line, which intersects the curve. The intersection point is \( (\alpha_1, T_{11}) (\alpha_1, T_{12}) \ldots \) The corresponding heating rate is \( \beta_1, \beta_2, \ldots \) Select another \( \alpha \) and repeat the above process, then another set of data \( (\alpha_2, T_{21}) (\alpha_2, T_{22}) \ldots \) can be obtained. The heating rate corresponding to them is still \( \beta_1, \beta_2, \ldots \)

Equation (4) can be transformed into:

\[
\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \exp\left( - \frac{E_a}{RT} \right) dT
\]  

For the curve of \( \beta_1 \), integrate (5) on both sides to get

\[
\int_{\alpha_1}^{\alpha_2} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta_1} \int_{T_{11}}^{T_{12}} \exp\left( - \frac{E_a}{RT} \right) dT
\]  

For the curve of \( \beta_2 \), integrate (5) on both sides to get

\[
\int_{\alpha_1}^{\alpha_2} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta_2} \int_{T_{21}}^{T_{22}} \exp\left( - \frac{E_a}{RT} \right) dT
\]  

Subtracting the above two formulas, \( \int_{\alpha_1}^{\alpha_2} \frac{d\alpha}{f(\alpha)} \) can be removed, so that the calculation of the reaction mechanism function can be avoided.

\[
\frac{A}{\beta_1} \int_{T_{11}}^{T_{12}} \exp\left( - \frac{E_a}{RT} \right) dT = \frac{A}{\beta_2} \int_{T_{21}}^{T_{22}} \exp\left( - \frac{E_a}{RT} \right) dT
\]  

Solving formula (8), the activation energy \( E_a \) of dry insulation equipment can be obtained.

3.2. Static method

For the field aging process of dry-type insulation equipment, the different aging stages are clearly separated. For one of the aging stages, the aging reaction is a single chemical reaction. The static method is a method for measuring the rate equation of a single chemical reaction and the relationship between the rate constant and temperature under the conditions of constant temperature and constant pressure.
For the premise of constant temperature and constant pressure, \( k(T) \) in equation (1) is a constant value that does not change with time and can be recorded as:

\[
k(T) = C
\]  

(9)

In the above formula, \( C \) is a constant.

The calculation method of the activation energy based on the static method is divided into the following two cases:

(a) When the reaction mechanism function is known, integrating equation (1) we get

\[
\int_{0}^{\alpha} \frac{d\alpha}{f(\alpha)} = k(T)t
\]  

(10)

Using the Arrhenius formula to describe \( k(T) \) in equation (10), we get

\[
\int_{0}^{\alpha} \frac{d\alpha}{f(\alpha)} = A\exp(-\frac{E}{RT})t
\]  

(11)

Because \( \alpha \) and \( t \) are known, and the reaction mechanism function \( f(\alpha) \) is also known, as long as two different sets of \( \alpha \) and \( t \) are taken, a binary equation system of chemical reaction activation energy \( E \) and pre-finger factor \( A \) can be obtained, so as to obtain Activation energy \( E \).

(b) The reaction mechanism function is unknown, and the same can be obtained by integrating equation (1).

\[
\int_{0}^{\alpha} \frac{d\alpha}{f(\alpha)} = k(T)t
\]  

(12)

When the reaction temperature is \( T_1 \), the selected reaction conversion rate \( \alpha \) and its corresponding time is \( t_1 \), and the above equation will become

\[
\int_{0}^{\alpha} \frac{d\alpha}{f(\alpha)} = k(T_1)t_1
\]  

(13)

When the reaction temperature is \( T_2 \), the selected reaction conversion rate \( \alpha \) and its corresponding time is \( t_2 \), and the above equation will become

\[
\int_{0}^{\alpha} \frac{d\alpha}{f(\alpha)} = k(T_2)t_2
\]  

(14)

Because it is the same reaction, the reaction function \( f(\alpha) \) is the same, and the conversion rate of the reaction is also the same. Then \( \int_{0}^{\alpha} \frac{d\alpha}{f(\alpha)} \) is equal. Subtracting the two equations can get

\[
k(T_1)t_1 = k(T_2)t_2
\]  

(15)

Using the Arrhenius formula to describe \( k(T) \) in equation (15), we get
By solving equation (16), the chemical activation energy $E$ of the reaction can be obtained.

4. Conclusion
This article analyzes the basic principles and experimental procedures of TGA, and proposes the main steps of thermogravimetric analysis of dry insulation equipment. Based on this, the principle of calculating the activation energy of chemical reactions is analyzed, and two effective methods for calculating the activation energy of dry insulation equipment are proposed. These methods provide a theoretical basis for the activation energy experiments, simulations, and field tests of dry-type insulation equipment.

Acknowledgments
This work was financially supported by SGCC Science and Technology Project "Research on Dry Insulation Equipment Defect Detection and Aging Evaluation Technology Based on Quantitative Characterization of Activated Energy" (KJ19-1-29).

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