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The dynamical admittance spectrometer: Instrument development and its application to chemical kinetics

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ABSTRACT

According to the intrinsic characteristics of the admittance spectrum, its application to kinetic research possesses some advantages. So in this report, based on the virtual instrument technology and infinitesimal principle, one dynamic admittance spectrometer was developed and primarily applied to the research of chemical kinetics. The hardware configuration mainly included five parts: signal generator, chemical system container, amplification circuit, data collecting circuit, the host computer and its application program. In order to realize the real-time dynamical test, two methods could be adopted, which were frequency response and time response (namely impulse response). It could be seen that the two methods were almost same for the chemical reaction system in this report. When the instrument was established, the measurement error of the instrument was tested through the matured commercial electrochemical workstation. It could be easily found that our dynamical spectrometer was better than the electrochemical workstation. Because the chemical reaction was continuous changing system, the infinitesimal principle was used to dynamical measurement. For the sucrose hydrolyzation system under acid, the time length for one infinitesimal was determined to be one second by experiments. Thanks to the characteristics of admittance, the catalyst hydrochloric acid was highly conducting and with little capacitance value, but the other reactants are highly insulating and with little conductance value. So when measuring capacitance value to represent the concentration of the reactants, the testing error can be ignored. Then the standard capacitance–concentration curve could be obtained. From the dynamically testing results and the standard capacitance–concentration curve, the function relationship between concentration of sucrose and reaction time could be obtained. At last, the kinetic equation of hydrolyzation of sucrose under HCl could be determined to be $r = -\frac{d[\text{sucrose}]}{dt} = kc_{\text{SU}}^{1}c_{\text{HCl}}^{1.46}$, with total reacting order of 2.46.

1. Introduction

Most of scientists in chemistry and materials used the commercial instruments to do their research. However, when the targets enter into the microscopic world such as the kinetics of elementary chemical reaction, common

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instruments always cannot satisfy the requirement. This may be the direct reason that the molecular beam technology could be invented. The kinetics of chemical reaction is one of the most basic fields of the chemistry and related science. The progress of the related instruments such as laser and molecular beams, combined with the quantum calculation, has taken the chemical kinetics into the elementary reaction. Also the related transition or resonance state could be investigated [1–4]. As to the research of macro kinetics in chemical reaction, especially for such reactions in chemical industry, the main target is to achieve the dynamical relationship between concentrations of reactants and the reaction time. As to the widely researched microstructure or nano-structure of materials, the key is the aggregation of molecules, which is also dynamical process. The basic characteristic of all the dynamical processes is that the parameters of the system are real-time changing. So whether to chemical reaction or molecule aggregation, the real-time dynamical instrument is needed to achieve the whole properties. However, in most cases, the real-time measurement instruments and the related measurement methods can ot satisfy the requirements of real-time test with high testing frequency, which makes the scientist has to do such research through manually testing the parameters at regular intervals, and of course, the testing error is large.

Up to now, the optical and electrical signals were broadly used in the testing instruments. When the researched system was superimposed small amplitude alternating voltage signal $u(t) = U_m \sin(\omega t)$, the current $i(t) = I_m \sin(\omega t + \theta)$ will be generated, where the $\omega = 2\pi f$, and θ is the phase difference between current and voltage. The ratio of current and voltage $Y = i(t)/u(t)$ is admittance, which is always been expressed in complex $Y \equiv G + j\omega C$, where the G is conductance, and C is capacitance. Plotting the Y to the frequency f can get the admittance spectrum. The reciprocal of admittance is impedance $Z = Z' + jZ''$. As to the complicated systems in chemistry such as chemical reaction or molecular aggregation, the physical meanings of the real and imaginary parts of impedance are not clear. But because it adopts the easy equivalent circuit for analysis, it is also widely applied. As the powerful electrical measurement methods, impedance and admittance have been widely used to chemistry and materials, surface, device and life science [5–13]. Presently, the dynamic optic spectrometers have already been developed such as transient absorption and photoluminescence spectrometers. However, their prices are expensive for the common laboratory. On the other hand, compared with optical signals, the electrical signal is greatly easier to be controlled because of the great progress of the modern electronic information technology. In spite of this, the application of the dynamical admittance spectrometer to the kinetics in chemistry or materials has not yet been reported.

According to the intrinsic characteristics of the admittance spectrum, its application to kinetic research possesses some advantages. Firstly, the data of admittance includes conductance and capacitance, which is the unique advantage because it could be used to test the conductor and insulator and thus the testing target is broad. Secondly, the researched system is perturbed by the small amplitude alternating sine signals, which is smaller than the thermal voltage. So this could avoid the obvious affection to the system and also leads to the linear relationship between the perturbation and the response of the system. And then the mathematic processing of the testing results could use the linear method. Thirdly, it also has the characteristics of the wide testing frequency range and highly sensitivity.

So in this report, based on the virtual instrument technology and infinitesimal principle, one dynamic admittance spectrometer was developed and primarily applied to the research of chemical kinetics. Combined with other microstructure topography instrument such as electron microscope, this real-time dynamical instrument could also been used to the application of dynamical research of microstructure of molecule aggregation.

2. The hardware of the dynamical admittance instrument

The dynamical admittance spectrometer was designed to dynamically measure the process of the molecule changing. The chemical system container and the corresponding connector were needed. Because the signals from signal generator were all small amplitude, the corresponding amplification circuit was necessary. The amplified signals were collected and transported by data acquisition card to host computer, then they were analyzed through the identification algorithm processed by our group. And at last, the kinetic equation for the molecule changing process could be achieved. In order to be simple, the simple hydrolyzation of sucrose was chosen to be the molecule changing system in this report. So the hardware configuration mainly included the following five parts (Fig. 1): signal generator, chemical system container, amplification circuit, data collecting circuit, the host computer and its application program.

The signal generator was programmed by LabVIEW, which controlled the D/A module of the data acquisition card to introduce the signal into the chemical system. In order to avoid the obvious affection to the system, the introduced signals were all small amplitude sine signals. After they were output from the chemical system, the signals were smaller because of the unavoidable signal absorption, which would be amplified by NE5532 amplifier. Then the signals are transported into the host computer through the data collecting card PXI-6070E from NI instrument Ltd. Inputting different signals into the chemical system, the outputting signals would be different. So according to the different inputting signals, the data processing software should be suitably programmed. Combining the corresponding system identification theory, the system parameters such as capacitance and conductance values could be achieved. The real appearance of the dynamical spectrometer could be seen in Fig. 2. But during the testing experiment, the chemical reacting container and the connecting electric wire were all placed into an iron shield box to avoid the electromagnetic inference of the environment.