



Two-channel and differential dielectric spectroscopy characterization of lubricating oil



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ABSTRACT

In this paper, two-channel and differential dielectric spectroscopy (TD-DES) measurement method has been proposed and the corresponding TD-DES Analyzer based on AD5933 impedance converter chip has been designed. Both of the theoretical analysis of TD-DES measurement and the TD-DES experimental results resulted from oxidation-series samples prepared by simulation oxidation and in-service series samples collected from different in-service equipments have proved that TD-DES method can improve the measurement sensitivity significantly. Two typical stages for lubricating oil degradation process including the homogeneous DSP stage and the heterogeneous interfacial stage have been discovered and verified by the TD-DES characteristics data analysis for the oxidation-series and in-service series samples, especially the aqueous Ox₁₃-series and Ox₁₄-series samples. Good linear relationships between TD-DES data and FT-IR peak areas for both oxidation-series and in-service series samples have been obtained with the correlation coefficients are all greater than 0.93. TD-DES is a new effective method for lubricating oil quality sensing.

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1. Introduction

Lubricating oil plays a key role in industrial and automotive equipments with the multiple enhancing functions such as sealing, lubrication, anti-friction, cooling, cleaning and anti-corrosion. It is important to evaluate the equipment working state by monitoring the quality of lubricating oil. Currently, the main methods for lubricating oil monitoring include atomic emission spectrometry (AES), atomic absorption spectrometry (AAS), ferrography, Fourier transform infrared spectroscopy (FT-IR), routine physical and chemical properties tests and electrical properties tests [1–5]. AAS, AES and ferrography focus on the analysis of the metal contaminants resulted from the moving parts. The degradation characteristics of the lubricating oil matrix are mainly determined by routine physical and chemical tests, FT-IR and dielectric properties tests. Routine physical and chemical properties tests mainly include determination of viscosity, total acid number (TAN), total base number (TBN), insolubles content (IC), fuel and water dilution, glycol contamination, etc. These tests are usually time-consuming and the validity and interpretation of their results are often ambiguous [6].

FT-IR monitoring parameters including oxidation, nitration, sulfation, water, additive depletion, soot and fuel have broadly been applied in rapid laboratory analysis of lubricating oil quality [3,7–16]. FT-IR analysis correlates well with chemical sensor responses such as shear transverse wave (STW) resonator [17] and TAN [3]. The major disadvantage of the FT-IR is its poor environmental adaptability, which makes FT-IR method not suitable for onboard and on-line measurement. Sensor application for oil degradation analysis based on FT-IR has not been reported so far. Physical and chemical sensors including viscosity measurement sensors, solid-state microsensors, electrochemical sensors, gas-phase measurement sensors, chemical recognition sensors, etc., have been proposed and developed to analyze the oil matrix degradation [18]. However it is very difficult to thoroughly explain the degradation process of the lubricating oil matrix because the oil matrix is a kind of complex mixture system. To some extent, it is impossible to predict the exact remaining useful lifetime of lubricating oil. What we are most concerned about is the current status of the lubricating oil matrix. So onboard assessment of oil quality is highly desirable in order to make a quick and accurate decision about oil change need [18].

Currently, dielectric and electrochemical properties analysis methods and their sensing application for lubricating oil quality monitoring have been paid more and more attention to, which can provide remarkable potential for direct analysis of complex

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lubricants with the advantages of simple instrumentation, rapid analysis process, comprehensive result interpretation and onboard monitoring ability. Dielectric spectroscopy (DES sometimes called impedance spectroscopy), and also known as electrochemical impedance spectroscopy (EIS), measures the dielectric properties of a medium as a function of frequency. It is based on the interaction of an external field with the electric dipole moment of the sample, often expressed by permittivity. Permittivity measurement by DES has widely been employed to monitor lubricating oil quality with the simple, rapid and comprehensive advantages [6,19–21]. DES or EIS as non-invasive and rapid analysis method plays an important role in electrochemistry, bioelectrical impedance, corrosion monitoring [22,23]. The internal structure, kinetic and electrical characterization of complex mixture systems by DES, especially the heterogeneous systems, is a new and promising interdisciplinary research field. DES is also playing an important role in analysis of polymers, colloidal dispersion, polymer membrane systems and biological cells system [24–27].

DES has been proved to be a useful tool for analysis of industrial lubricants and can offer the opportunity to characterize, evaluate and provide insights into mechanisms of lubricant performance and degradation. Lvovich et al. [6] has analyzed the EIS characterization of industrial lubricants draining from engine field tests provided by the Lubrizol Corporation in the frequency range from 10 MHz to 1 MHz. The adsorption-desorption and diffusion of surface active industrial lubricant additives (mostly detergent-dispersant) on the electrode has also been analyzed by higher harmonic non-linear electrochemical impedance spectroscopy (NLEIS) [19]. A detailed EIS study on a complex time-dependent mechanism of water-oil interactions has also been presented [28]. Large agglomerates with the size depending on mixing and interaction with the oil additives, mostly detergents, will form when water was injected into oil. The EIS study of carbon black based model systems in the frequency range from 10 MHz to 10 Hz has demonstrated that the complex mechanism of interaction between charged carbon black particles and surfactants (primarily dispersants) was responsible for maintaining dispersions in engine oils [29]. Dielectric and electrochemical devices can offer a wide range of sensors for measuring lubricating oil quality and it has been shown that they can be engaged in determining different stages of degradation [18]. Sensor analysis based on dielectric and electrochemical properties have been shown practical for automotive oil condition monitoring nowadays [18,20,30–32].

Dielectric and electrochemical sensing of degraded oil mostly relies on measuring polarity due to oxidative stress and different contaminants including water, fuel, ethylene glycol antifreezing agent, etc. The sensors based on dielectric and electrochemical properties are usually simple, well fabricated and utilized. For example, two parallel plate electrodes and interdigitated electrodes capacitor sensors are the main sensor technologies [20,33]. Compared with the chemical sensors, the dielectric and electrochemical sensors can avoid deterioration and aging of the sensitive layer imprinted on the sensor surface while their selectivity will be diminished. So a combination of DES with multivariate data analysis has been explored [6,18–20,34]. Although multivariate chemometrics methods represented by the partial least squares regression (PLSR) can explained the DES data more efficiently than normal algorithms, the weak characteristic differences and their change trends during oil degradation must be explored by more effective measurement techniques. So the two-channel and differential DES (TD-DES) measurement method has been proposed in this article which can obtain the characteristic differences between different oil systems effectively.

Moreover, the lubricating oil systems were normally regarded as heterogeneous systems such as water-in-oil emulsion based on inverse micelles and colloidal dispersion of carbon black in

the previous publications [29]. The heterogeneous systems are the mixture systems which have interfaces where materials of different electrical properties contact each other [24]. The characteristic polarization mechanism of the heterogeneous system is the interfacial polarization that is due to the build-up of charge on the interfaces, which is not suitable for the lubricating oil analysis to some extent.

Here, we propose the dielectric submicroscopic phase (DSP) feature to explain and understand the lubricating oil matrix and its degradation process. The formation process and reasons of the DSP for lubricating oil matrix can be explained as follows. Functional additives in lubricating oil system are typically composed of a polar functional group and long non-polar hydrocarbon “tail” chain that allows the additives to become compatible with non-polar base oil [6]. Polar additives often exist in lubricants in the form of inverse micelles with polar head groups forming the internal phase and external hydrocarbon tails keeping micelles suspended in base oil. As for the fresh oil, the relative aggregations based on inverse micelles due to the polarity and molecular size differences between the polar additives and the non-polar base oil will form in the lubricating oil matrix. As for the used oil, oil deterioration is mainly due to the inner oxidation-induced degradation and external contaminants. During the early oxidation-induced degradation, oxidation by-products composed of polar functional groups (such as aldehydes, ketones, and carboxylic acids) and non-polar hydrocarbons are similar to the oil additives inverse micelles in the fresh oil. These early oxidation by-products can interact with chemically active oil additives such as dispersants, detergents (surfactants) and be prevented from further aggregation. So the relative aggregations based on inverse micelles will form and exist in both fresh and used lubricating oil matrix. The dimension of the relative aggregation is between microscopic molecule and macroscopic interface dispersed phase, that is to say, the lubricating oil systems containing the aggregations are not heterogeneous systems indeed. The morphology and dispersion characteristics of the relative aggregations in the lubricating oil are named by the dielectric submicroscopic phase (DSP) by us, which well correlates with the homogeneity and stability of the lubricating oil system.

It is believed by us that the DSP and heterogeneous interfacial features can be used to explain the degradation process of lubricating oil system. In the early oxidation-induced degradation, the DSP of the lubricating oil system will form. As the further oxidation-induced degradation, chemical polymerization reactions will take place among the aggregation by-products and macromolecular compounds will be generated gradually. At this stage the DSP will be damaged gradually as the chemically active oil additives depletion and more and more aggregations will form in the lubricating oil system. Oxidation by-products and increasing presence of external contaminants such as soot, water, fuel, wear debris, or airborne particles will destroy the DSP status and the lubricating oil system will develop into the heterogeneous interfacial system in the end.

DES has been employed to analyze the strong heterogeneous interfacial features in the in-service lubricating oils [6,35], which have interfacial polarization characteristics induced by colloidal aggregates. These colloidal dispersion or emulsification systems are mainly affected by post-oxidation degradation products (carbon black, sludge, etc.) and external contaminants (water, fuel, coolant, etc.). Ulrich et al. [36] has explored the combination of EIS and multivariate data analysis to simultaneously predict the concentrations of soot and diesel in engine oil with the frequency range from 600 kHz to 20 Hz. It was proved that EIS characteristics contained information about soot and diesel content. But the differences in the dielectric/impedance values were not so distinct that the multivariate data analysis should be used.

Because the relative aggregations are only a fraction of the whole lubricating oil matrix, the dielectric/impedance responses for the

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