Total harmonic distortion spectroscopy for kinetics analysis and diagnosis of fuel cells and electrolyzers

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Fuel cells and electrolyzers are important for the renewable energy conversion and storage to combat global warming and to strengthen national energy security, both of which have pronounced dynamic response to changes in current for the complex anode oxidation and cathode reduction kinetics. Dynamic electrochemical methods as such have more advantages over steady state measurements due to the enabled frequency- response information in the kinetics analysis and system diagnosis [1]. Electrochemical impedance spectroscopy (EIS) is a commonly used, dynamic and frequency response method operating in a linear range, which is achieved by applying small excitation amplitude to a target system [2]. However, since the nonlinearity of the target system is neglected, EIS can hardly treat the full complexity of an electrochemical system. Therefore, extracting nonlinear response information has been recognized as an effective way to identify the electrochemical reaction mechanism [3–13].

Fig.1 illustrates a schematic diagram of the voltage response of a direct methanol fuel cell (DMFC) to a large-amplitude excitation current of sinusoidal form. The voltage response is displayed in both time domain and frequency domain. In the frequency domain, besides the response at the fundamental frequency, i.e. frequency of the excitation current, voltage contributions at the frequencies of higher harmonics are also observed. The voltage intensity at the fundamental frequency is the linear part of the system response, which is used to calculate the linear frequency response of DMFC, i.e. EIS. However, the responses at the higher harmonic frequencies are the nonlinear

contribution of the system response, which can be used for evaluating nonlinearity and identifying reaction kinetics for complex electrochemical systems [11,12].
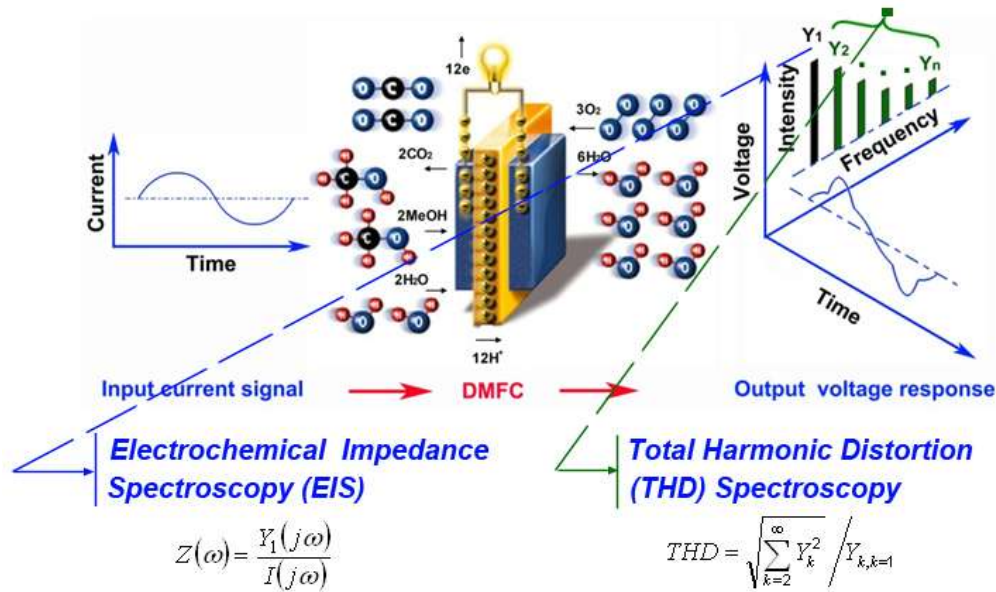

Fig.1 Schematic diagram of the voltage response of a DMFC in both time domain and frequency domain to a large-amplitude excitation current of sinusoidal form

THD spectroscopy is an effective method to evaluate nonlinearity of the target system that considers the contribution at all higher harmonic frequencies. It can be defined as the ratio of the Euclidean norm of the system response Y of all higher harmonic frequencies ($k \geq 2$) to that of the fundamental frequency ($k = 1$) [11]:

$$THD = \frac{\sqrt{\sum_{k=2}^{\infty} Y_k^2}}{Y_1} \quad (1)$$

In DMFCs, the predominantly THD decreases monotonously in intensity with decreasing methanol concentration in the frequency range from 0.1Hz to 0.63Hz [11,12]. The observed correlation between dynamic fuel cell behavior and inlet concentration enables the use of THD for sensorless detection of the methanol concentration level in DMFC systems (as shown in Fig.2) [11]. Simulation studies on the dynamics of various anode kinetic models [12] support a three-step methanol oxidation mechanism developed previously [14].
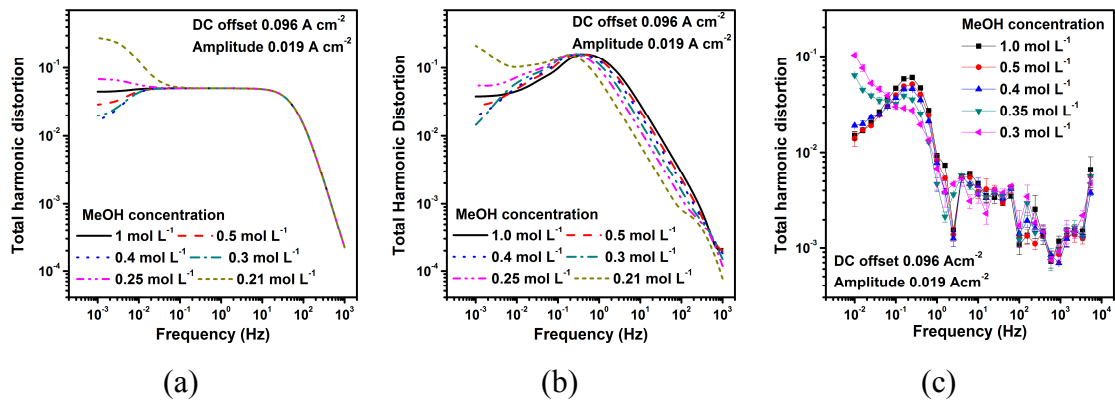
Fig.2 THD spectra of the DMFC anode (a) Simulated THD spectra for methanol one-step oxidation mechanism, (b) Simulated THD spectra for methanol three-step oxidation mechanism with Kauranen-Frumkin / Temkin kinetics, (c) Experimental results in half cell mode [12]

Oxygen reduction reaction (ORR) also exerts predominant influence on the dynamic response behavior for both DMFC and PEMFC. Therefore, a thorough understanding of the ORR mechanism and its proper mathematical description are the keys for the system diagnostics and control as well as the electro-catalyst selection and optimization for fuel cells. Figure 3 shows the simulated THD spectra of the PEMFC with different ORR kinetics and O_2 stoichiometry and the experimental one. With the help of experimental validation, the frequency range from 2.5 Hz to 15.8 Hz is recognized to be ORR kinetics sensitive in the THD spectroscopy. The Damjanovic ORR mechanism with oxygen chemisorption is comparable to the reality because it better reproduces experimental results [13].
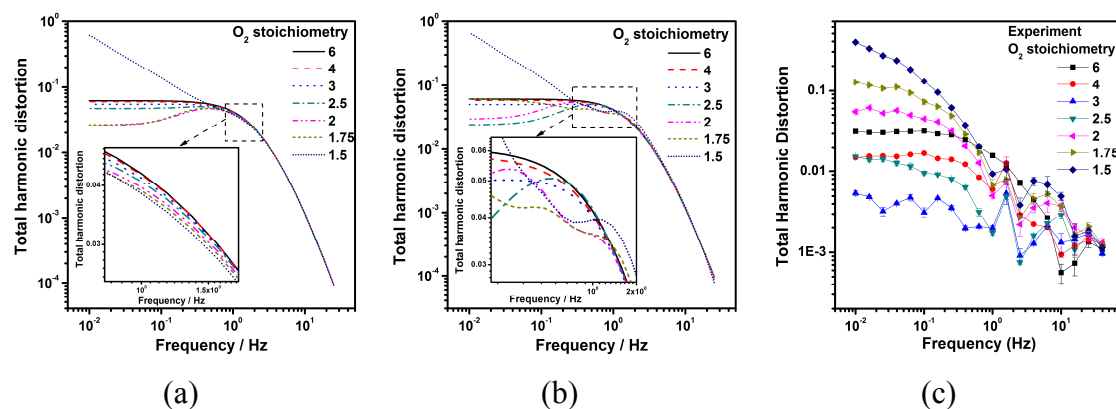
Fig.3 THD spectra of the PEMFC with different O_2 stoichiometry at 60°C: (a) Simulated results for Damjanovic ORR mechanism with oxygen electrochemisorption (b) Simulated results for Damjanovic ORR mechanism with oxygen chemisorption (3) Experimental results [13].

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