Review

Application of electrochemical impedance spectroscopy in bio-fuel cell characterization: A review

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Diwakar Kashyap [a], Prabhat K. Dwivedi [b], Jitendra K. Pandey [a],
Young Ho Kim [c], Gyu Man Kim [d], Ashutosh Sharma [b], Sanket Goel [a,*]

[a] University of Petroleum and Energy Studies (UPES), Dehradun 248007, India
[b] Department of Chemical Engineering, Indian Institute of Technology, Kanpur 208016, India
[c] Medical Device Development Center, Daegu-Gyeongbuk Medical Innovation Foundation, 88 Dongnae-ro, Dong-gu, Daegu, Republic of Korea
[d] School of Mechanical Engineering, Kyungpook National University, Daegu 702-701, Republic of Korea

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ABSTRACT

Fuel cell is an efficient energy conversion device converting chemical energy directly into electrical energy. It is a fact that, to boost the fuel cell performance, resistance (charge transfer resistance, mass transfer resistance and electrolyte resistance) should be decreased. For this, many techniques have been used for cell testing such as: cyclic voltammetry, current interruption measurement, chronoamperometry, chronopotentiometry, polarization curve and electrochemical impedance spectroscopy (EIS). Among these techniques, EIS is a well-established, non-intrusive, non-destructive, semi-quantitative, and an efficient technique for identification of each circuit element. In this review article, application of electrochemical impedance spectroscopy in identification of individual components of total resistance and their dependence on different factors in biofuel cell along with some recent advancement in this technique have been discussed.

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Introduction

Fuel cell is an efficient energy conversion device that converts chemical energy directly into electrical energy. The power output of a fuel cell depends on many factors, such as kinetics of reaction, fuel flow rate, operating temperature, internal resistance, and electrical load. While high conversion efficiency (>80%) is the main advantage of fuel cell, slow kinetics, high internal resistance and fuel crossover are few downsides that limit power output from these devices [1,2]. Many techniques such as: Cyclic Voltammetry, Polarization Curve, Chronopotentiometry, Chronoamperometry, Current Interruption, and Electrochemical Impedance Spectroscopy (EIS),

have been used for testing and diagnose of fuel cells with each technique having its own advantages and disadvantages [3–8]. The overall internal resistance of a fuel cell has many contributors such as electrode resistance, electrolyte resistance, charge transfer resistance, double layer capacitance, mass transfer resistance and other ohmic losses. In order to enhance the performance of fuel cell and draw optimum power, identification of different components of total internal resistance and its mitigation is necessary. These contributors of total internal resistance can't be reduced using a single strategy. Separation of the individual contributors helps to optimization fuel cell performance by assisting to optimize cell fabrication methods, catalyst loading, and membrane thickness [9–11].

The cyclic voltammetry is most commonly used technique to study redox reaction. In this technique the direction of potential is swiped between two fixed points and the resulting current is recorded. The capacitive current affects the sensitivity of cyclic voltammetry measurements, so normal and differential pulse voltammetry have been developed to reduce the effects of capacitive currents during measurement [4,12]. In current interruption technique ohmic load is immediately released and the resulting decrease in potential with time is recorded. This technique is used to measure the total internal resistance of cell, but it is not able to differentiate between the ohmic resistance, mass transfer resistance and kinetic effects, and only suitable for systems in which ohmic resistance is dominant [13]. In polarization measurement, cell potential is plotted against current under load. The internal resistance of a fuel cell is inversely proportional to the power density and can be calculated from the slope of polarization curves [14]. All of the above mentioned techniques are not able to identify the individual components of total internal resistance and measurement is also affected by non-faradaic component (double-layer charging of electrode/electrolyte interface) to different extent. EIS is a non-destructive and powerful technique capable of providing information about all resistive, capacitive, and inductive contributors in short period of time using appropriate equivalent circuit model. In addition to its potential application in analysis of electrochemical systems such as: fuel cell, batteries, corrosion, and sensors, recently this technique has also been used in a variety of applications, such as to study sol gel synthesis, reverse osmosis, catalysis

and determination of critical micelle concentration [15–17]. Different techniques used for fuel cell testing has been compared in Table 1.

Fundamental of EIS

Resistance is the ability of circuit element to hinder the flow of electrons. Ohm's law, used to calculate the resistance, is only applicable to an ideal circuit; that shows linearity and independent of frequency. Unlike resistance, impedance depends on frequency. In order to measure impedance of a circuit element a small alternating current (AC) is applied and corresponding potential is measured as a function of frequency. The initial impedance measurement was performed to determine the capacitance of ideally polarizable electrodes and alternating current polarography [18,19]. A small AC current and corresponding potential is represented by following equations:

$$E_t = E_o \sin(\omega t) \tag{1}$$

$$I_t = I_o \sin(\omega t + \phi) \tag{2}$$

$$\text{Impedance } (Z) = \frac{E_t}{I_t} = \frac{E_o \sin(\omega t)}{I_o \sin(\omega t + \phi)} \tag{3}$$

EIS can be performed in two or three electrodes system, whereby the three electrode system used to analyse electrochemical reaction at one electrode, in which one electrode (anode/cathode) acts as working electrode and other electrode works as counter electrode, and measurement is done against the reference electrode. Two electrodes system is used for performance analysis of a complete cell, in which one electrode acts as working electrode and other counter electrode. The current flowing at an electrified interface, in an electrochemical reaction, contains both faradic as well as non-faradaic components. The faradic component arises from the electron transfer reaction and non-faradaic current results from double layer capacitance. Solution resistance, charge transfer resistance, mass transfer resistance and polarization resistance are the main Faradaic components. Impedance of common circuit element is shown in Table 2.

Table 1 – Comparison of different techniques used for fuel cell testing.		
Techniques	Advantages	Disadvantages
Cyclic voltammetry	(a) Most extensively used technique to study redox reaction.	(a) Capacitance current and back ground charging current are the main problems in normal cyclic voltammetry. (b) The ratio of the peak faradaic current to the charging current decreases with increasing voltage
Current interruption	(a) Used to determine internal resistance of electrochemical system (b) Easy to recognize measurement errors associated with magnetic and galvanic coupling.	(a) Only show total ohmic drop across the electrode and only suitable for system in which ohmic resistance is dominant (b) Not able to differentiate charge transfer, mass transport and other ohmic losses
Polarization curve	(a) Provides information on the performance losses in the individual cell or stack under operating conditions (Fuel flow rate, humidity, temperature, load)	(a) Underlying mechanism is difficult to analyse, because different contributors of potential drop overlap.
EIS	(a) Able to separate different contributors of total internal resistance (Charge transfer, mass transport, electrolyte resistance)	(a) Only applicable to steady state or quasi steady state systems (b) Data analysis is difficult using basic fitting models.