A novel Central Composite Design based response surface methodology optimization study for the synthesis of Pd/CNT direct formic acid fuel cell anode catalyst

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ABSTRACT

At present, carbon nanotube supported Pd catalysts are synthesized via $NaBH_4$ reduction method to investigate their electro catalytic activity thorough formic acid electro oxidation. In order to optimize the synthesis conditions such as %Pd amount (X_1), $NaBH_4$ amount (times, X_2), water amount (ml, X_3), and time (min., X_4), Central Composite Design (CCD) experiments are designed and determined by the Design-Expert program to determine the maximum observed current (mA/mgPd). Formic acid electro oxidation current density of the catalyst is computed by the model as 974.80 mA/mg Pd for the catalyst prepared at optimum operating conditions (41.14 for %Pd amount, 280.23 $NaBH_4$ amount, 26.80 ml water amount, and 167.14 min time) obtained with numerical optimization method in CCD. This computed value is very close to the experimentally measured value as 920 mA/mg Pd. Finally, formic acid fuel cell measurements were performed on the Pd/CNT catalyst prepared at optimum operating conditions and compared with the commercial Pd black and Pt black catalysts. As a result, Pd/CNT exhibits better performance compared to Pd black, revealing that Pd/CNT is a promising catalyst for the direct formic acid fuel cell measurements.

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Introduction

Fuel cells which convert chemical energy directly to electrical energy are potential substitution of fossil fuels thanks to being eco-friendly and having high efficiency [1,2]. There are different types of fuel cells such as proton exchange membrane fuel cells (PEMFCs), direct methanol fuel cells (DMFCs) [3,4], direct ethanol fuel cells (DEFCs) [5–7], direct formic acid fuel cells (DFACs) [8–14], phosphoric acid fuel cells (PAFCs) [15], alkaline fuel cells (AFCs) [16], solid oxide fuel cells (SOFCs) [17], molten carbonate fuel cells (MCFCs) [18]. DFAFCs have great potential for portable power generators due to their higher theoretical open circuit potential as 1.45 V than 1.23 V for DMFCs [19].

Pt and Pd catalysts have been widely evaluated for formic acid electroooxidation reaction [20]. CO poisoning is one of the crucial obstacle for commercialization of fuel cells because it causes not only deceleration the formic acid electro oxidation reaction but also high anode over potential [21]. CO poisoning and expensive price of Pt prevent the commercialization DEFCs employing Pt anodes. Pd anode is regarded as a strong alternative to Pt anode due to its relatively cheap price and less CO poisoning [10,14,22−25]. Formic acid electro oxidation usually proceeds on dehydrogenation pathways over Pd based catalysts, revealing that the formic acid is directly oxidized to CO_2 without forming carbonaceous species [26,27]. However, the main drawback of Pd anodes like durability through the formic acid electrooxidation leads to introduce second or third metal to improve formic acid electrooxidation activity [28−33].

Metal loading, particle size of the catalyst and the nature of support materials influence the electrooxidation activity of the catalyst, called as structure sensitivity [4,34,35]. Fundamental studies on the mechanisms of electro-oxidation are imperative to reveal the mechanisms of electrooxidation, the nature of the site, and poisoning species for improved design of these catalysts. Electrocatalytic oxidation rates of CO, methanol, and ethanol strongly depend on the structure of the catalyst. The electro-catalytic oxidation of CO on Pt single crystals is a structure sensitive process and the rates were shown to increase in the order Pt (111) < Pt (100) < Pt (110) [36,37]. Perez et al. [38] investigated the effect of particle size effect on ethanol oxidation on carbon supported platinum catalysts in the Pt particle size range from 2.2 nm to 3.6 nm both in half-cell and in a single DEFC. The specific activity for ethanol oxidation presented a maximum at a Pt particle size of 2.5 nm. Geng and Lu [39] reported that there was a significant size effect on the activity of electro-oxidation of carbon monoxide in alkaline solution when different sized gold nano-particles were used. It was observed that the ultra fine metal particles (2 and 6 nm Au) were more active than the larger ones (12, 24, and 41 nm). Vulcan XC 72R carbon-black based electrocatalyst is commonly employed as anode and cathode catalyst of fuel cells. However, carbon-black support leads to low catalyst utilization due to its structural density [5]. There are several properties that a suitable support should possess as high surface area, good electrical properties, and high electrochemical stability. Carbon nanotubes (CNTs) are attractive as electrode material candidates due their excellent properties as good chemical stability and large surface area [40].

Structural characteristics and electronic properties such as degree of alloying and oxidation state could be modified depending on the synthesis method to improve on the electro catalytic activity [41,42]. Sodium borohydride ($NaBH_4$) reduction and modified polyol reduction method are the commonly used methods for the synthesis of carbon nanotube supported Pd nanoparticles [43−46]. Considering the polyol reduction method, surfactants such as poly vinyl pyrrolidone (PVP) and sodium dodecyl sulfate (SDS) are usually employed as stabilizing agent, strongly adsorbed on the surface of Pd nanoparticles [47,48]. For the $NaBH_4$ reduction method, the obtained Pd particles exhibit a broad size distribution because nucleation and growth steps occur at intermediate stages of particle formation. Although, there are many studies devoted to formic acid electro oxidation studies, experimental design

based response surface methodology method has not ever been used to optimize the synthesis conditions of Pd/CNT catalysts for the formic acid electro oxidation reaction. The objective of this study is to optimize the synthesis conditions for Pd/CNT formic acid electro oxidation catalysts.

Conventionally, optimization has been carried out by monitoring the effect of one parameter on the process at a time. Based on this traditional method, only the parameter to be examined is varied, while the other parameters are held at a constant value. However, this process has many disadvantages: it neither clarifies the interactive effects among the parameters examined, nor does it produce statistical data explaining more detailed effects of the parameters on the response (the experimental result). In addition, these methods require numerous experiments, consuming not only a great deal of time but also large amounts of chemicals [49]. In recent years, to overcome these shortcomings, response surface methodology (RSM), a powerful optimization method, has been widely used to optimize the most effective process conditions in the presence of fewer experimental data. This method has recently been studied for the purposes of optimization [50,51]. Among the reasons for its popularity are the fact that it does not require the consumption of extra chemicals for each parameter, it is less time-consuming, and less cost- and labor-intensive [52−54]. RSM employs a mathematical algorithm based on experimental results generated from experiments designed by a program, and validation of the quadratic model is derived from statistical techniques. Linear or quadratic polynomial functions are used to describe the system under investigation and, ultimately, to explore (by modeling and displacing) experimental conditions up to optimization. In RSM, the independent variables that affect the system are selected based on the aim and experience of the researcher by means of a literature search. Next, the experimental design is selected and the experiments are performed according to the selected experimental matrix and the experimental data obtained undergo mathematical-statistical treatment using a polynomial function. The suitability of the model is then assessed and optimal values are obtained for each variable studied [49]. The main advantages of RSM are that all the parameters studied for optimization vary at the same time and that it is a mathematical model which incorporates experimental data. As a result, the number of experiments required for optimization using RSM is less than that required by conventional methods.

Herein, Pd/CNT catalysts were prepared by $NaBH_4$ reduction method. First of all, Pd/CNT supported catalysts were prepared at different Pd: $NaBH_4$ mole ratios, % Pd weight percentage, and water amount used during the synthesis, and mixing time to optimize synthesis conditions through the formic acid electro oxidation reaction. Formic acid electro oxidation measurements were performed in 0.5 M H_2SO_4 + 1.0 M HCOOH solution via cyclic voltammetry (CV). Among the programs in RSM, Central Composite Design (CCD) is the most popular program used to obtain a second-order model describing the experimental system. CCD experiments designed and determined by the Design-Expert program were performed to determine the maximum observed current (mA/mgPd) and to evaluate the effects of the parameters investigated, %Pd amount (X_1), $NaBH_4$ amount (times, X_2), water amount (ml, X_3), and time (min., X_4) on the