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Performance of a novel non-platinum cathode catalyst for direct methanol fuel cells

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ABSTRACT

Currently, platinum is used as the cathode catalyst in direct methanol fuel cells (DMFCs). However, platinum reduces the number of active sites for the oxygen reduction reaction (ORR) due to the reaction between platinum and methanol and the strong adsorption of carbon monoxide molecules on the platinum surface, and in addition, platinum is very expensive. Hence, this study proposes cobalt phthalocyanine/carbon-tungsten oxide nanowires ($W_{18}O_{49}$) as a non-platinum catalyst for the cathode side of a DMFC. We determined the kinetic parameters of the catalyst and investigated the factors affecting the reaction. The factors involved in the examination of the significant parameters were the synthetic method, the pyrolysis temperature, the mass ratio of CoPc to carbon, the mass ratio of CoPc/C to tungsten hexachloride and the molarity of tungsten hexachloride. The optimum parameters were determined to be a pyrolysis temperature of 600 °C and a mass ratio of CoPc/C:WCl_6 of 1.90. These conditions produced a peak potential at 0.63 V vs. RHE, a mass activity of 1.76 A $g^{-1}_{catalyst}$ at 0.65 V, an average electron transfer number of 3.9 with water as the main product, and an electron transfer number of 3.9 at 0.65 V. Finally, the results showed that the non-platinum catalyst (which is less expensive than platinum) has similar characteristics to platinum. The single cell performance test showed that the power density is 9.0 mW cm^{-2}. The catalyst has comparable performance with other macrocycle catalysts with modified structures.

1. Introduction

Fuel cells are a source of alternative energy proposed to replace fossil fuel-based energy sources. Fuel cell operation involves the use of a fuel to convert chemical energy to electrical energy. Several types of fuel cells have been proposed, including polymer electrolyte membrane fuel cells (PEMFCs), solid oxide fuel cells (SOFCs), alkaline fuel cells, molten carbonate fuel cells, and direct methanol fuel cells (DMFCs). Fuel cells are advantageous because of their low emissions during electricity generation (thereby reducing local air pollution) and because they can provide enhance energy security [1,2]. One type of fuel cell that has increasingly shown promise for small appliances, such as cell phones, cameras, and laptops, is the DMFC, which uses methanol as the fuel. DMFCs offer the following advantages in small appliances: high energy density, low pollution, few safety concerns, rapid start-up, low weight, simplicity, small size, and easy charging [3]. Despite these advantages, there are some drawbacks of DMFCs that must be overcome prior to commercialization [4].

One of the drawbacks of a DMFC is the sluggish kinetics of the reaction at the cathode side of the fuel cell. An oxygen reduction reaction (ORR) occurs at the cathode side of a DMFC, while a methanol oxidation reaction (MOR) occurs at the anode side. Platinum catalysts are commonly used as cathode catalysts in DMFCs. Platinum has a high selectivity for ORR and MOR [5]. The crossover of methanol from the anode to cathode in a DMFC results in a combination of ORR and MOR at the cathode side and slows the kinetics of the reactions at the cathode side. Using platinum also reduces the number of active sites available for ORR because the by-product of MOR, namely, carbon monoxide, adsorbs strongly on platinum catalysts [6]. Moreover, the high cost of platinum hinders the commercialization of DMFCs [7–9]. The development of a non-platinum catalyst is needed to overcome these drawbacks.

ORR has two reaction pathways: either 2-electron transfer, which produces hydrogen peroxide, as in reaction (1), or direct 4-electron transfer, which produces water, as in reaction (2) [10].

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (1)$$

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Nomenclature

α	electron transfer coefficient in the rate-determining step for oxygen reduction
β_0	constant term
β_i	linear effect term
β_{ii}	quadratic effect term
β_{ij}	interaction effect term
C_0	oxygen concentration at the electrode surface (for low current density and oxygen saturated electrolyte, $C_0 \approx 1.3 \times 10^{-6}$ mol cm^{-3})
D_{O2}	O_2 diffusion coefficient (cm^2 s^{-1})
E	experimental disk potential (V vs. RHE)
E^0	thermodynamic electrode potential under the experimental conditions (V vs. RHE)
F	Faraday's constant (96, 485 C mol^{-1})
i_d	experimental disk current (mA/cm^2)
i_r	experimental ring current (mA/cm^2)
i^o	exchange current density or the current density in the absence of net electrochemical reactions and at zero overpotential (mA/cm^2)
i_k	kinetic current density of the ORR (mA/cm^2)
k_e	electron transfer rate in the rate determining step (cm/s)
N_r	collection coefficient of the ring electrode
n	number of electron transfer in oxygen reduction reaction (e)
n_α	electron transfer number at the rate determining step
R	universal gas constant (8.314 J mol^{-1} K^{-1})
T	absolute temperature (K)
v	kinetic viscosity of the solution (0.01 cm^2 s^{-1})
ω	rotation rate of the disk electrode (rad/s)
x_i and x_j	real or coded variables
y	response variable

$$O_2 + 4H^+ + 4e^- \rightarrow H_2O \qquad (2)$$

The formation of hydrogen peroxide should be avoided, as the formation of hydrogen peroxide creates a toxic environment for the membrane by destroying the chemical bonding of the catalyst to membrane. A desirable catalyst for ORR would take the 4-electron transfer route [11].

Many studies have investigated the replacement of platinum in DMFCs, and one reported replacement is a macrocycle catalyst [10]. There are several types of macrocycles, such as porphyrin (P), phthalocyanine (Pc), tetramethylphenylporphyrin (TMPP), phenanthroline complexes and others [10]. These macrocycle catalysts have different capabilities to reduce oxygen, depending on whether they are metal-based macrocycles. Changes in the structure of the macrocycles also contribute to changes in the ORR activity [12]. Cobalt phthalocyanine (CoPc) was chosen because it is highly inert to methanol; however, this catalyst has low reactivity towards ORR [13,14]. CoPc tends to produce hydrogen peroxide, compared to other macrocycles. In a previous study, CoPc/C demonstrated great promise when supported on tungsten oxide nanowires; the catalyst functions primarily through a 4-electron transfer reaction, producing water as the by-product instead of hydrogen peroxide. A theoretical study showed that tungsten atom adsorption on CoPc can improve the adsorption energy and thus lead to reaction pathways that produce water as the main product [13].

Some previous studies have prepared macrocycle catalysts for ORR. Temperature is one of the main factors in preparing macrocycle catalysts that are active towards ORR. Some macrocycle catalysts used for ORR require a specific pyrolysis temperature to realize activity towards ORR. Other research groups [14–20] have examined pyrolysis temperatures ranging from approximately 100–1000 °C, and the results showed that the best pyrolysis temperature range is approximately 700–800 °C [14,18,20]. Some other studies fixed the pyrolysis temperature at 600 °C [21], 800 °C [22–24], or 950 °C [25]. Other important factors in the preparation of a catalyst for ORR are the ratios of CoPc to carbon and CoPc/C to nanowires. It is crucial to determine the ratio that will give the best ORR performance. The ratio of macrocycle to carbon reported in the literature varies from as low as 0.24 [15], 0.7241 [22], 1 [14,26,27], 1.9411 [25], 2 [28], or 3 to as high as 4 [21]. The report with the lowest ratio of 0.24 stated that the best catalytic temperatures are approximately 500 °C and 700 °C; however, with a ratio of 0.7241, the resulting peak potential approaches 0.7 V vs. NHE, and the electron transfer number ranges from 3.0 to 3.5. It is well known that iron-based macrocycles have higher ORR activity than cobalt-based macrocycles. Even using a mass ratio of macrocycle to carbon of 1, iron-based macrocycles have higher ORR activity [25–27]. Kruusenberg et al. [14] also tested the ratio of metal phthalocyanine and porphyrin to MWCNT of 1, obtaining an electron transfer number of less than 3 for metal phthalocyanine.

Additional studies have focused on the ratio of metal loading to carbon [19,20,23,24]. Zhang et al. [20] used a ratio of metal loading to carbon as low as 0.10 and obtained an electron transfer number as high as 3.85. Meanwhile, in a separate study [24], a ratio of total metal loading to carbon of almost 0.2 resulted in an electron transfer number of 3.8. Both studies used catalysts with better molecular structures than CoPc, leading to the increase in the electron transfer number of the reaction. Xu et al. [29] used a ratio as high as 0.74 of metal loading to carbon with CoPc/MWCNT as the catalyst. This catalyst results in a low electron transfer number of 1.7–1.8. A ratio of metal loading to carbon as high as 0.74 can be used to block the active sites on the catalyst; otherwise, agglomeration of the catalyst will occur. The best ratio of metal loading to carbon is approximately 0.3, as this value results in a high electron transfer number in the ORR [19,23]. Other studies have used a ratio of macrocycle to support catalyst as low as 0.1764 [18] and as high as 12.210 [17]. Some of the previously mentioned studies used carbon as a support for the catalyst. The use of metal oxides, such as titanium oxide, as support catalysts has recently increased due to their unique properties. The solvothermal method is used for nanowire synthesis because this method can control the morphology of the nanowires [30]. Previous studies have shown that nanowires can be formed with dimensions ranging from 2 nm to 10 nm [30–34]. However, only Sun et al. [35] have tested the effects of a solution concentration from 0.003 M to 0.007 M on the nanowire structure. The authors claimed that the diameter of the nanowires remained the same, even as the concentration changed; however, increasing the molarity did affect the length of the nanowire bundles.

Other fields have studied the optimization of catalyst preparation using response surface methodology [36,37], while in the study of ORR, most researchers have used the one-factor-at-a-time (OFAT) method. Jeng et al. [38] investigated the activity of a ruthenium-selenium (RuSe) catalyst supported on carbon nan-