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Synthesis and electrochemical characterization of binary carbon supported Pd₃Co nanocatalyst for oxygen reduction reaction in direct methanol fuel cells

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ABSTRACT

Binary carbon supports are applied to make the membrane electrode assembly (MEA) of passive direct methanol fuel cells (PDMFCs) and their comprehensive electrochemical characterization is considered. Electrocatalytic properties for the oxygen reduction reaction (ORR) are evaluated using polarization curves and electrochemical impedance spectroscopy (EIS) in PDMFC. The best efficiency is obtained when the mass ratio of multi-walled carbon nanotubes (MWCNTs) and Vulcan XC-72R (VC) is 25:75. The results of the electrode kinetic parameters indicate that introduction of MWCNTs as a secondary support delivers high available surface area, good electronic conductivity, and fast ORR kinetics. In addition to the significant role of Pd₃Co active surface area on kinetic of the system, the improvement of kinetic parameters is also associated with the decrease of activation energy for ORR on binary-support electrode resulting in a notable enhancement of kinetic parameters. An 8-h lifetime test is performed for the single cell to evaluate the durability in which the MEA is made using MWCNT/VC with the mass ratio of 25:75. The test results show that the mentioned ratio of MWCNT and VC support results in highest stability and durability.

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Introduction

Direct methanol fuel cells (DMFCs) offer lots of promise as the next-generation power source for portable equipment [1,2]. Specifically, a passive air-breathing DMFC system consisting of an anode that uptake methanol from the built-in reservoir and a cathode that “breathes” from the

atmosphere works without any auxiliary devices [3–5]. Methanol is an attractive fuel because: firstly, methanol is a liquid and therefore it can be effortlessly transported and stored and also can be dispensed within the current fuel mesh. Secondly, methanol is inexpensive and abundant [4,6]. However, further development of the DMFC is still facing some technical problems, amongst which methanol crossover is the most significant obstacle. However, the

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permeation of methanol through the membrane produces a loss of efficiency and a decrease of the fuel cell voltage due to methanol oxidation at the cathode, which remain one of the major problems for the DMFC performance [7,8]. In DMFCs, when Pt is used as the cathode catalyst, the difficulties are exacerbated by methanol crossover from the anode that results in a mixed potential at the cathode [9–11]. Therefore, a non-Pt catalyst with high activity and selectivity toward ORR is urgently required. Recently, extensive studies have been carried out on the feasibility of replacing Pt with substitute metals such as Pd, the cost of which is only one-fifth of Pt [12,13]. Pure palladium is less expensive than Pt but its electrocatalytic actions for ORR is at minimum five times lower than of Pt. For this reason, great efforts have been devoted to improve the Pd electroactivity by alloying it with transition metals like Co, Fe, and Ni [9,14]. In specific, PdCo/C electrocatalysts have been identified as hopeful alternatives to Pt catalysts for ORR, and the use of these electrocatalysts is believed to be a feasible solution to the methanol crossover problem in direct methanol fuel cells (DMFCs) [15,16]. Over the past years, much research was done to lowering metallic catalyst loading and electrode over potential losses. Apart from activity of the electrocatalyst, type and properties of the carbon support, such as its hydrophobicity [17], surface area [18], electronic conductivity [19] and surface functional groups [20,21], all contribute to the overall performance of the GDE [22]. Carbon is not only used to conduct electrons in a GDE, but also should outcome in the presence of macro- and microscopic pores [23] and helps to stabilize the three-phase boundary and morphology. Various types of carbon and graphite, such as Vulcan [21,24,25], black pearl [22,26], acetylene black [26,27], Ketjen black carbon [27], Iranian carbon black [28], graphite nanofiber [17], carbon nanotube [29,30], high-surface-area carbon nanohorns [31], treated carbon blacks and other materials such as ionic and electronic conductive polymers [32] have been applied as single supports in investigation of the oxygen reduction reaction (ORR) in GDEs. The Vulcan XC-72 carbon black has been the greatest used carbon support in fuel cells. However, blocking of the oxygen transportation decreases the reactive sites to get on high current densities. When carbon black is used as electrocatalyst support [33], new shapes of carbon materials such as graphite nanofibers (GNFs) [17] and carbon nanotubes (CNTs) [34,35] were also investigated as catalyst supports. Carbon nanotubes (CNTs) have been demonstrated to possess high electronic properties, good chemical stability, and large surface areas. These exceptional properties make carbon nanotubes very suitable for supporting metal nanoparticles in many potential uses ranging from advanced catalytic systems to very complex electrochemical sensors to highly efficient fuel cells [36]. However, when using a single carbon support, it might difficult to obtain the optimal parameters needed for enhancing the gas diffusion performance of the ORR, as well as to obtain optimized ionic and electronic conductivity, good morphology, surface area, electron diffusion and product removal. Sakaguchi et al. [37] and Watanabe et al. [38] first reported the usage of binary carbon supports in liquid electrolyte fuel cells. Wang et al. [22] and Gharibi et al. [39–41] reported the use of binary carbon supports with dissimilar surface areas.

In this paper, MWCNTs are first used as a secondary carbon support of Pd₃Co catalyst layers at different mass ratios in order to control the best mass ratio of these types of carbon in acid media at the presence and absence of methanol and afterwards for fabricating membrane electrode assembly (MEA) in passive direct methanol fuel cells (PDMFCs). The role of binary carbon supports in the electrocatalyst is evaluated and characterized through consideration of polarization curves and electrochemical impedance spectroscopy (EIS). It will be shown that by using two carbon supports, the electrochemical performance of as-formed MEA can be enhanced. This improvement is further exemplified by enhanced electrode kinetics of ORR in the presence of methanol for binary carbon support electrode compared to that with single support. Surface area changes of single and binary-support electrodes were evaluated by means of an accelerated durability test (ADT). Finally, stability of electrodes was moreover studied in PDMFC and compared with that of the commercial Pt/C catalyst.

Experimental section

Materials and synthesis of electrocatalysts

The chemical compounds of concentrated sulfuric acid, Pd [NO₃]₂·2H₂O, Co [NO₃]₂·6H₂O, ethylene glycol, methanol, 2-propanol were bought from Merck; Nafion solution 5% from Aldrich; Vulcan XC-72R (VC) from Cabot, and multi-walled carbon nanotubes (MWCNTs) from Plasma Chem. GmbH. Since MWCNTs are chemically inert, the MWCNTs (5–20 nm) were functionalized by pretreatment with 70% nitric acid in order to introduce surface oxides before preparation of the composites [42–45]. In our study, the MWCNTs were refluxed under constant agitation at 120 °C in concentrated nitric acid for 12 h. The solid phase filtered and washed with distilled water and the improved functionalized MWCNTs were then dried at 80 °C for 12 h.

Pd₃Co electrocatalysts were prepared by impregnation on MWCNT and/or VC in different mass ratios reduced by the action of ethylene glycol. The procedure for synthesis of electrocatalysts was as follows: the support was first dispersed in distilled water and 2-propanol by treating in an ultrasonic bath for 1 h. Pd [NO₃]₂·2H₂O and Co [NO₃]₂·6H₂O were added to this ultrasonicated suspension in various atomic ratios of Pd to Co under constant stirring for a total metal loading of 10%wt. For regulating the pH of this mixture to over 10–11, a few drops of 1.0 M NaOH solution were added to the mixture before adding the reducing agent. The resulting mixture was filtered, washed with double distilled water and acetone and afterwards dried in an oven at 80–100 °C to obtain the supported catalyst powder.

Ink preparation

For the diffusion layer, a mix of 30%wt PTFE and 70%wt VC in 2-propanol and water was sonicated for 30 min with a sonicator (Misonix model S-3000) for production a uniform suspension. The suspension was decorated onto the carbon paper (TGPH-0120T) and the electrode was dried in oven at 120 °C for

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