

NICKEL DEPOSITION EFFECTS ON THE GROWTH OF CARBON NANOFIBERS ON CARBON PAPER

S. Celebi^{*1)}, J. van der Schaaf¹⁾, T.A. Nijhuis¹⁾, F.A. de Bruijn²⁾ and J.C. Schouten¹⁾

¹⁾ Laboratory of Chemical Reactor Engineering, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
Email: s.celebi@tue.nl; website: www.chem.tue.nl/scr

²⁾ Energy Research Centre of The Netherlands (ECN), P.O. Box 1, 1755 ZG Petten, The Netherlands

Summary

Carbon nanofiber (CNF) growth has been achieved on carbon paper fibers via two nickel deposition routes: i. nickel nanoparticle-ethanol suspension casting, and ii. homogenous deposition precipitation (HDP) of nickel onto carbon paper. Nickel nanoparticles created regular tubular CNF whereas HDP of nickel forms mainly herringbone and platelet fiber structures. Average porosity of the carbon paper maintained over 50 % in both methods having more than 20 % CNF growth on one side of the carbon paper.

Keywords

Fuel Cells, Materials for energy applications, Alternate energy

Introduction

Alternative catalyst supports for Proton Exchange Membrane Fuel Cells (PEMFCs) are investigated for two main reasons: a. lowering the voltage loss as caused by oxygen transport limitations, and b. increasing the resistance towards corrosion. A more graphitic¹, highly oriented carbon combines high electronic conductivity with an acceptable surface area of the support which improves Pt utilization and yields a PEMFC electrode with enhanced stability, when compared with current (more amorphous) carbon supports. Carbon nanofibers (CNFs) are one example of such a more controlled support structure (Figure 1), whose integration into carbon paper gas diffusion layer (GDL) is explored in this study.

Experimental

Growth of carbon nanofibers was investigated by two nickel deposition methods: i. nickel nanoparticle attachment by casting the ethanol nanoparticle suspension, and ii. homogenous deposition precipitation (HDP) of nickel. Nickel nanoparticles were synthesized at 60 °C by hydrazine reduction of nickel ions in the presence of cetyltrimethylammonium bromide (CTAB). Dried and washed nanoparticle powder was suspended in ethanol having 0.1 wt%. 5 ml of suspension was directly dried on carbon paper (4.0 cm in diameter paper with 190 µm thickness) inserted on a teflon holder. In HDP of nickel, nickel ions obtained by dissolving nickel nitrate hexahydrate are deposited by the aid of urea

decomposition at 90 °C for 24 hours. After drying overnight at 80 °C, a 9.0 micron leaf structured nickel hydroxide layer is formed on the surface of carbon fibers (these fibers are 5-8 µm carbon fibers which forms carbon paper) as was confirmed by SEM analysis. With the nanoparticle method, nickel nanoparticles are attached to the surface as nanocrystals forming a random dense distribution as was observed by SEM analysis. Nickel loadings on the carbon paper are controlled separately and a deposition mask system is introduced in both nickel deposition methods. Oxidation of the carbon paper was not required in both deposition methods since the number of oxygen groups is sufficient to form the required nickel clusters or nickel leaf layers.

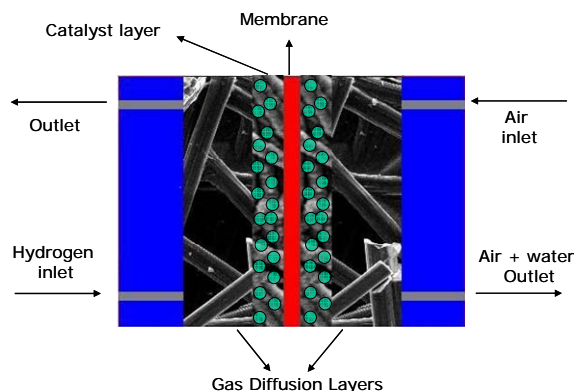


Figure 1. CNF-integrated PEM fuel cell

* To whom all correspondence should be addressed

Results and Discussion

CNF formation by the nickel nanoparticle casting method creates tubular fibers of 15 nm size whereas HDP of nickel forms mainly herringbone CNFs of 20 nm with an angle of 40° to the growth axis and a considerable amount of 80-150 nm platelet fibers are formed. In HDP of nickel, the nickel reduction at 500 °C by hydrogen (balanced by nitrogen) transforms nickel hydroxide layers to nickel nanoclusters without changing the leaf formation on the surface. The CNF growth mechanism using the HDP method is determined as “octopus-like” growth in HDP which is in agreement with a previous study performed on carbon felt². The CNF growth mechanism in case of the nickel nanoparticle casting method is found as “tip-growth”³. The BET surface area of the CNF integrated carbon papers by HDP of nickel and nickel nanoparticle casting are measured as 57 m²/g (30% CNF loading) and 50 m²/g (27% CNF loading) on carbon paper, respectively (Table 1). Taking into account the loading and the surface area of the carbon paper (0.2 m²/g), the BET area of the CNF was calculated as 176 m²/g for HDP of nickel and 185 m²/g for nickel nanoparticle casting. The increase in the thickness of the carbon paper by the CNF layer reduces the porosity of the carbon paper, 78% to 55% with HDP of nickel, and to 65% with the nickel nanoparticle casting method. These results are also confirmed by the SEM pictures shown in Figure 2.

The shell thickness of the CNF for the nickel nanoparticle casting method is smaller than in the case of HDP of nickel in spite of the fact that the growth times are the same. The reason for the smaller increase in the shell thickness of the carbon fibers in case of the nickel nanoparticle casting method may be the nanofiber density on the surface. For HDP of nickel, the shell thickness increases with 80% before CNF growth and reduction of this leaf layer creates more dense nickel active faces which make a grafted CNF layer. For nickel nanoparticle casting, CNFs are growing from the carbon fiber surface and nickel deactivation takes place after a critical fiber length estimated as 2 microns. Therefore, for nickel nanoparticle casting, thinner carbon nanofiber thickness is obtained with respect to HDP of nickel.

The deposition of nickel determines mainly the structure of the CNFs on the GDL which might be used as a water management layer instead of a degradable polymer layer used in the current technology or a direct catalyst layer for platinum adsorption in PEM fuel cells. Since the catalyst layer thickness in PEM fuel cells generally is of 5-10 micron, it may be better to use nickel nanoparticle casting to create thinner rounded CNF networks on GDL.

Conclusions

The synthesis of alternative gas diffusion media for application in PEMFC electrodes, consisting of a 10 µm CNF layer on one side of a macroporous carbon paper has been demonstrated. The effect of two different nickel

deposition methods on the CNF growth is presented. CNFs can be used both as microporous layer in gas diffusion media to control water management, as well as support for platinum nanoparticles, with potentially an enhanced stability against carbon corrosion and a better Pt utilization.

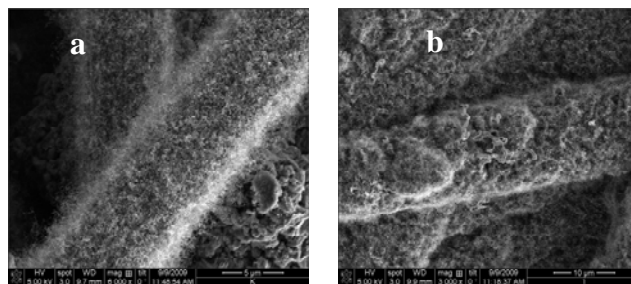


Figure 2. a) Carbon nanofiber growth on carbon paper by a) nickel nanoparticle casting b) Homogenous deposition precipitation of nickel.

Table 1. Effect of the nickel deposition methods on CNF integrated carbon paper surface characteristics.

Results	i. Nickel nanoparticle casting	ii. HDP of nickel
CNF loading on carbon paper (mg/mg) %	27	30
Total BET, m ² /g	50	57
CNF BET, m ² /g	185	176
CNF-carbon paper porosity, %	65	55

Acknowledgements

This work was part of the Dutch EOS-LT Consortium PEMFC (EOSLT 06005 and EOSLT 07005) supported by the Ministry of Economic Affairs.

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