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G Ercolano, S Cavaliere, D Jones, J Rozière. Electrospun Ni nanofibres as Pt supports for PEMFC electrodes. ECS Transactions, 2015, 69 (17), pp.1237-1242. 10.1149/06917.1237ecst . hal-01252818

HAL Id: hal-01252818

<https://hal.science/hal-01252818>

Submitted on 8 Jan 2016

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Electrospun Ni nanofibres as Pt supports for PEMFC electrodes

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Nickel nanofibres were prepared by electrospinning followed by specific thermal treatments. Pt/Ni fibrous electrocatalysts were obtained by galvanic displacement of the metal surface atoms with platinum. A novel, very fast Ni displacement assisted by microwaves is described. The Pt/Ni nanofibres were characterised for their activity towards oxygen reduction for their application in PEMFC electrodes.

Introduction

Reduction of the fabrication and material costs and improved durability are pivotal issues to a successful market introduction of Proton Exchange Membrane Fuel Cells (PEMFC) (1). A more effective utilisation of the Pt catalyst and the use of more durable supports are the core of the development of novel, market ready PEMFC (2,3).

Electrospinning is a scalable technique for the elaboration of nanowires of metals and metal oxides (4). The capability to finely control the diameter and composition of the nanowires makes this technique of interest in the search for novel catalyst support materials and morphologies (5,6). We are interested in the possible paradigm shift from Pt nanoparticles supported on carbon to atomic layers of platinum (7) deposited on metals that could be achieved by coupling electrospinning to electrochemical Pt deposition techniques such as galvanostatic displacement of Ni (8,9).

In this work, nickel nanofibres were prepared by electrospinning and their surface atoms exchanged by galvanic displacement with Pt to obtain Pt/Ni fibrous electrocatalysts that are characterised for their electrocatalytic properties. A novel very simple and fast approach of microwave-assisted Ni displacement is described, allowing the reduction of process duration from hours to ≤ 1 minute.

Experimental

Preparation of Ni nanofibres

Nickel nanofibres were produced by electrospinning followed by thermal treatments. A 10 %_{wt} solution of polyvinylpyrrolidone (PVP) and nickel acetate (1:1_{wt}) in ethanol and dimethylformamide (7:3_{vol}) was electrospun at 1 kV cm⁻¹ on a Linari Biomedical rotating drum collector combined with a syringe pump (KP Scientific) and a high voltage power supply (Spellman HV). The PVP carrier polymer was removed from the fibres by calcination at 600 °C in air during which the nickel salt was converted to nickel oxide. The calcination was conducted adopting a multistep ramp with dwells at 150 °C and 250 °C to reduce mechanical stress and ensure that the resulting nickel oxide would keep the original fibrous morphology. The calcined nanofibres were later reduced at 300 °C in an Ar/H₂ atmosphere (H₂ content 5 %) for 12 hrs.

Pt deposition onto nickel nanofibres

Platinum was deposited on the nickel nanofibres using two different approaches: a Simple Galvanic Displacement (SIGD) method adapted from a previous work (9) and a novel Microwave Assisted Galvanic Displacement Acceleration (MAGDA).

The same exchange solution was adopted for both approaches: 20 mg of chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) were dissolved in 6 ml of H_2O and the pH was adjusted to 7 using sodium hydroxide. The Pt containing solution was then added to 40 ml of N_2 saturated H_2O containing 20 mg of nickel nanofibres. A complete exchange would lead to 30 % platinum loading.

For SIGD, the solution was stirred at room temperature for 48 hrs, while in MAGDA the solution was stirred for 60 sec in a microwave (MW) reactor (MiniFlow 200SS Sairem) at 200 W. The temperature reached after the 60 sec MW process was $\sim 55^\circ\text{C}$. At the end of both exchange processes the nanofibres were collected by filtration and carefully washed with ethanol and water.

Characterisation of the (Pt)/Ni nanofibres

The morphology of the electrospun materials before and after Pt deposition was characterised by scanning electron microscopy (SEM) using a FEI Quanta FEG 200 equipped with energy-dispersive spectroscopy analysis (EDS) and transmission electron microscopy (TEM) using a JEOL 1200 EXII.

X-ray diffraction (XRD) patterns of the Ni supports were recorded at room temperature in Bragg-Brentano configuration using a PANalytical X'pert diffractometer, equipped with a hybrid monochromator, operating with $\text{CuK}\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$), and using a step size of $0.1^\circ 2\theta$ in the 2θ domain from 20 to 80° .

Electrochemical characterisation was carried out in a conventional three-electrode cell consisting of a glassy carbon rotating disk electrode (RDE) (working electrode, geometric area of 0.196 cm^2), a reversible hydrogen electrode (reference electrode, RHE) and a platinum wire (counter electrode). A Pine bipotentiostat model AFCBP1 was used. All the potential values are referred to the RHE. Inks were prepared dispersing 5 mg of catalysed support in $300 \mu\text{L}$ of isopropanol, $20 \mu\text{L}$ of water, and $15 \mu\text{L}$ of 5 wt % Nafion. These inks were then deposited onto the RDE surface with a micropipette to give a final Pt loading of $\sim 100 \mu\text{g}\cdot\text{cm}^{-2}$. (The SIGD had loading $\sim 25 \mu\text{g}\cdot\text{cm}^{-2}$ due to the low Pt content; for MAGDA, complete exchange was hypothesized and 30 wt% loading was used in the calculation). Cyclic voltammetry was carried out at 100 mV/s in N_2 saturated 0.1 M aqueous HClO_4 and the electrochemical surface area (ECSA) of platinum was calculated by integrating the peak of hydrogen desorption from the Pt sites. Oxygen reduction reactions (ORR) were conducted on a RDE in an oxygen saturated 0.1 M HClO_4 aqueous electrolyte at increasing rotating speeds ($400, 900, 1600, 2500 \text{ RPM}$) chosen in order to achieve equally spaced saturation currents (Koutecky-Levich).

Results and discussion

Preparation and characterisation of Ni nanofibres

The SEM images in Figure 1 show the nanofibres at the different stages of the synthesis and demonstrate how the fibrous morphology is successfully maintained despite the large volume variation resulting from the polymer removal and later by the nickel

oxide reduction to metallic nickel. Fig. 1 a in particular shows that using optimised electrospinning deposition conditions and solution composition leads to defect-free nanofibres. The diameter is reduced by half during the reduction step, passing from 300 to 150 nm (Figures 1 b and c, respectively).

Figure 1. SEM images of a) PVP–nickel acetate, b) nickel oxide and c) nickel nanofibres

The XRD analysis on the calcined and reduced nanofibres (Figure 2a and b respectively) show that the former correspond to nickel oxide, while the latter are not yet completely metallic Ni, since a residual ~ 5 % of the nickel is still in the oxide form. A longer reduction treatment or possibly a more aggressive reduction atmosphere will be implemented to completely reduce the nickel. It is important to notice that the XRD provides evidence for the presence of two separate phases (Ni and NiO), and not for an oxygen doped nickel or a nickel suboxide. It could be argued that the vast majority of the grains forming the fibres are pure metallic nickel and a small residual amount of grains are still nickel oxide.

Pt deposition and characterisation of Pt/Ni nanofibres

Nickel nanofibres were coated with Pt using a Simple Galvanic Displacement (SIGD) method and a Microwave Assisted Galvanic Displacement Acceleration (MAGDA).

The solution appearance after 48 hrs SIGD was rather unchanged, maintaining the initial yellow tint and intensity, while after the 60 sec of MAGDA the solution had become completely transparent, suggesting that all the platinum had been removed from solution.

The TEM images in Figure 3 show platinum nanoparticles that are uniformly dispersed onto the metal wires, but no evidence for continuous film formation. The platinum loading for the SIGD samples estimated by EDS was ~ 5 %, vastly smaller than the 30 % expected were exchange to be complete.

Cyclic voltammetry in N₂ saturated 0.1 M HClO₄ for the Pt_{SIGD}/Ni (not presented) showed the presence of uncovered nickel (oxidation peak at ~ 0.45 V) as well as steadily increasing corrosion currents in the 1.0 V - 1.2 V range. Both of these features are absent in the cyclic voltammetry of the sample obtained *via* MAGDA.

Figure 2. XRD analysis of a) nickel oxide and b) nickel nanofibres

Figure 3. TEM micrographs of platinum on nickel nanofibres after the SIGD (a) and the MAGDA process (b).

ECSA calculated from the cyclic voltammetry were $42 \text{ m}^2\text{g}^{-1}$ for the $\text{Pt}_{\text{SIGD}}/\text{Ni}$ and $21 \text{ m}^2\text{g}^{-1}$ for the $\text{Pt}_{\text{MAGDA}}/\text{Ni}$. The first is consistent with Pt nanoparticles of $\sim 5\text{-}7 \text{ nm}$ in diameter, while the ECSA of the MAGDA Pt/Ni sample indicates the presence of large platinum particle agglomerates with a size of $\sim 18\text{-}20 \text{ nm}$ as observed in the TEM micrographs in Figure 3. The fact that nickel does not seem to be exposed could be taken as an indication that a continuous/contiguous coverage of platinum is more likely.

The activity of the Pt/Ni nanofibres towards ORR was evaluated in acidic medium. From the oxygen reduction currents reported in Figure 4 it is evident that the SIGD sample evolves during the experiment, as the diffusion limited currents are not equally spaced, indicating that the sample capability to reduce oxygen is quickly decreasing.

The calculated mass activities at 0.9 V were 12 A/g and 42 A/g for the $\text{Pt}_{\text{SIGD}}/\text{Ni}$ and $\text{Pt}_{\text{MAGDA}}/\text{Ni}$ respectively, and the mass activity of the latter is higher than $\text{Pt}_{\text{SIGD}}/\text{Ni}$ in all the evaluated range.

Figure 4. ORR at 5 mVs⁻¹ in 0.1 M HClO₄ saturated with O₂ at 400, 900, 1600, 2500 RPM a) Pt SIGD/Ni, b) Pt MAGDA/Ni

Conclusion

This work reports a simple and easily up-scalable method to produce Ni nanofibres covered with Pt, by combining electrospinning and galvanic displacement. The simple Pt deposition method (SIGD) was improved and quickened by the application of microwaves (MAGDA). The electrocatalytic characterisation showed a better activity towards ORR of the sample prepared via the MAGDA approach. Further studies *ex situ* and *in situ* on the electrocatalyst durability are in progress to assess the applicability of Pt/Ni fibrous metallic nanomaterials in PEMFC.

Acknowledgments

The research leading to these results has received funding from the European Research Council under the European Union's Seventh Framework Programme (FP/2007–2013)/ERC Grant Agreement no. 306682.

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