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Corrosion Resistant Electrospun Niobium Carbide Nanotube Supports for PEMFC Cathodes

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A synthesis route is reported based on the electrospinning technique that leads to NbC nanotubes with the appropriate properties for an electrocatalyst support for PEMFC cathode. The NbC nanotubes were successfully catalysed with 3 nm Pt particles by a microwave assisted polyol method so as to be investigated as electrocatalyst support. The accelerated stress test (AST) described in this contribution highlights the high stability of the novel NbC based support in comparison with a commercial 50 % Pt/C with similar the electrochemical surface area (ECSA).

Introduction

Proton exchange membrane fuel cells (PEMFC) are promising energy conversion devices¹. However, to facilitate their widespread adoption, several issues remain, such as the stability of the cathode to oxidation on high potential excursions, which needs to be significantly improved^{2,3}. In some fuel cell operation conditions, carbon black electrocatalyst supports suffer from corrosion, leading to the aggregation, migration and detachment of electrocatalyst nanoparticles resulting in a loss of performance^{4,5}. Recent research has shown that metal carbides including niobium carbide can present the required properties in term of electrical conductivity and stability in acidic media to replace the electrocatalyst supports conventionally used in PEMFC^{6,7}. One of the remaining challenges is to design a support material with a morphology that will provide high surface area and adapted porosity^{8,9}. Electrospinning¹⁰ is a simple and versatile technique for the elaboration of 1 D nanostructures that have demonstrated unique electrical properties and high specific surface area¹¹ promoting both high platinum dispersion and gas accessibility. An innovative composition and controlled morphology are both keys for increasing the stability and the performance of the catalyst support.

We describe here the elaboration of NbC nanotubes obtained by electrospinning, and their catalysation with platinum nanoparticles through a microwave assisted polyol method¹². The electrocatalytic activity, the electrochemical surface area (ECSA) and its stability as assessed by accelerated stress test (AST) are reported and compared to those of a commercial 50 % Pt/C.

Experimental

Synthesis of NbC nanotubes

1.8 g of ammonium niobate oxalate (ANO) $(\text{NH}_4)_3[\text{NbO}(\text{C}_2\text{O}_4)_3] \cdot 2\text{H}_2\text{O}$ were dissolved in 5 g of distilled water and mixed with 4 g of ethanol containing polyvinylpyrrolidone (PVP, Mw 1,300,000, Aldrich). The ANO/PVP composite fibres were prepared by electrospinning the solution at 15 kV and at a flow of 0.2 mL/h. The collected ANO-PVP composite fibres were heated in air at 600 °C for 3 h to remove the carrier polymer. The resulting Nb_2O_5 fibres were then heated at 1100 °C in 10 % CH_4/H_2 at a flow rate of 100 mL/min. until Nb_2O_5 was totally converted to NbC, determined by monitoring the successive reactions¹³ with the TCD signal of a Micromeritics ASAP 2010 Chemi System.

Characterisation of NbC nanotubes

The sample morphology was characterised by scanning electron microscopy using a FEI Quanta FEG 200 SEM and by transmission electron microscopy using a JEOL 1200 EXII TEM. Powder X-ray diffraction (XRD) patterns were recorded at room temperature in Bragg-Brentano configuration using a PANalytical X'pert diffractometer, equipped with a hybrid monochromator, operating with CuK_α radiation ($\lambda = 1.541 \text{ \AA}$), and using a step size of $0.1^\circ 2\theta$ in the 2θ domain from 10 to 80 °. Thermogravimetric analysis (TGA) using a Netzsch STA 409 PC apparatus was performed to determine the fraction of residual carbon contained in niobium carbide nanotubes. The residual carbon content was confirmed by CHNS elemental analysis.

Pt particles synthesis and deposition

A microwave-assisted polyol method was used to synthesise Pt nanocatalyst particles¹². 70 mg of hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 99.9 % Alfa Aesar) were dissolved in 50 mL of ethylene glycol (99.5 %, Fluka) and the pH adjusted to pH 11 using 1 M NaOH solution (98 %, Sigma Aldrich) in ethylene glycol. The resulting solution was heated at 120 °C for 6 minutes in a microwave reactor (MiniFlow 200SS Sairem). A suspension containing 40 mg of the NbC nanotubes in 5 mL ethylene glycol was added to the as-synthesised Pt nanoparticle suspension and the pH adjusted to 2. After gentle stirring for 24 hours, the product was recovered by filtration, washed with milli-Q water and ethanol and dried overnight at 80 °C. The loading of platinum (as measured by scanning electron microscopy – energy dispersive x-ray spectroscopy (SEM-EDX)) on the niobium carbide nanotubes (including any residual carbon) was 30 wt%. This value was confirmed by X-ray fluorescence (XRF) using a Panalytical Axios max with a 4 kW X-ray tube with Rh anode.

Electrochemical characterisation

The *ex situ* electrochemical analyses were 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. A catalyst ink was prepared using standard methods and the following materials: 10 mg of Pt/NbC; 35 μL Nafion (5 %) (Aldrich); 1 mL water (milli-Q water); and 4 mL isopropanol (Aldrich). 6 - 10 μL of the catalyst ink (depending on the Pt loading) were deposited onto the electrode to give 6 μg_{Pt} /electrode. Cyclic voltammetry was carried out at 50 mV/s in N_2 saturated HClO_4 (0.1 M solution) and the electrochemical surface area (ECSA) of the platinum catalyst was calculated by integrating the peak corresponding to desorption of hydrogen from the Pt sites. An accelerated stress test (AST) was performed to investigate the stability of the catalysed supports by monitoring the ECSA over prolonged cycling. Cyclic voltammetry was carried out between 0.03 V and 1.2 V for 3000 cycles at 500 mV/s. Every 100 cycles, two cycles were performed at a slower rate of 50 mV/s and the ECSA calculated from them.

Results and discussion

Synthesis and physical characterisation

Composition: NbC was clearly identified as the only crystalline phase in the X-ray diffraction pattern of the NbC nanotubes (Figure 1). The amount of residual carbon was investigated by thermogravimetric analysis via a calibration that links the mass variation with the NbC/C ratio¹⁴; the proportion of the amount of residual carbon over the total amount of NbC and residual carbon was 4 wt%. This residual carbon might be formed during the carburation by decomposition of CH_4 at high temperature.

Figure 1 X-ray diffraction profile of the NbC nanotubes obtained after the carburation step.

Morphology: FEG-SEM (Figure 2) shows hollow 1D structures with porous walls, that could be an asset for the accessibility of the reactants to the catalyst³. An external average diameter of 160 nm for the nanotubes was measured.

Figure 2 SEM micrographs of the NbC nanotubes.

Electrocatalyst deposition

Platinum particles were synthesised and deposited on the NbC nanotubes with a weight Pt loading of 30 % (determined by SEM-EDX and XRF). A homogeneous dispersion of the particles with an average diameter of 3.1 nm was observed by TEM (Figure 3).

Figure 3 TEM micrograph of NbC nanotubes catalysed with Pt nanoparticles.

Electrochemical characterisation

Electrochemical characterisation was performed on Pt/NbC nanotubes and 50 wt% Pt/C (Alfa Aesar) used as reference. Cyclic voltammetry was carried out at 50 mV/s in N₂ saturated HClO₄ (0.1 M solution) and the electrochemical surface area (ECSA) of the platinum catalyst was calculated by integrating the peak corresponding to desorption of hydrogen from the Pt sites¹⁵ (Figure 4).

Figure 4 Cyclic voltammetry of 30 % Pt/ NbC supports and 50 % Pt/C in N₂ saturated HClO₄.

Cyclic voltammetry comprising 3,000 cycles up to 1.2 V was performed to investigate the stability of the catalysed supports, and the ECSA loss was evaluated¹⁶. The results are given in Figure 5. The initial ECSA of the 30 % Pt/NbC nanotubes was slightly lower than that of 50 % Pt/C (43 m²/g vs 52 m²/g). However the 30 % Pt/NbC nanotubes showed significantly greater stability to electrochemical corrosion since on voltage cycling to 1.2 V the ECSA was reduced by only 12%, compared with a loss of 25% for the Pt/C. The decrease in ECSA can be explained by two simultaneous phenomena related to the catalyst and its support: platinum particles degradation (involving Pt detachment, Pt dissolution/precipitation and Oswald ripening) and the corrosion of the support (also involving catalyst detachment)^{17,18}. Furthermore, a thin layer of Nb₂O₅ at the surface of the NbC nanotube sample was identified by XPS analysis¹⁹; this oxide layer possibly protects the support from further oxidation. Further analyses are planned to study any eventual progression of the oxide towards the core of the material.

Figure 5 Stability of the ECSA of the catalysed supports during the accelerated stress test to 1.2 V.

Conclusion

This work reports for the first time a synthesis route for the elaboration of niobium carbide nanotubes with porous walls. The support was catalysed with 3 nm Pt particles using a microwave-assisted polyol method. The electrochemical characterisation through accelerated stress test of the supported platinum particles reveal that this novel support is highly stable compared to a commercial 50 % Pt/C with similar ECSA. Further characterisation such as the *in situ* characterisation of this electrocatalyst support are planned to confirm this trend.

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