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Novel niobium carbide/carbon porous nanotube electrocatalyst supports for proton exchange membrane fuel cell cathodes

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HIGHLIGHTS

- NbC nanostructures with porous 1D morphology have been prepared by electrospinning.
- NbC porous tubes have been used as Pt nanoparticle supports for PEMFC electrodes.
- Pt/NbC demonstrates electroactivity towards oxygen reduction reaction.
- Pt/NbC is more stable than commercial Pt/C over prolonged cycling at high potential.
- Pt/NbC has been characterised in PEMFC at the cathode side with promising results.

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ABSTRACT

Niobium carbide/carbon nanotubular porous structures have been prepared using electrospinning and used as electrocatalyst supports for proton exchange membrane fuel cells. They were functionalised with 3.1 nm Pt particles synthesised by a microwave-assisted polyol method and characterised for their electrochemical properties. The novel NbC-based electrocatalyst demonstrated electroactivity towards the oxygen reduction reaction as well as greater stability over high potential cycling than a commercial carbon-based electrocatalyst. Pt/NbC/C was integrated at the cathode of a membrane electrode assembly and characterised in a single fuel cell showing promising activity and power density.

1. Introduction

Proton exchange membrane fuel cells (PEMFC) are efficient and clean energy conversion devices having automotive, stationary and portable applications [1]. In some fuel cell operation conditions including start/stop cycles and fuel starvation, carbon black electrocatalyst supports suffer from electrochemical corrosion, which can lead to the migration and aggregation, and/or detachment of electrocatalyst nanoparticles resulting in an early failure [2,3]. The preparation of materials with alternative chemical compositions and controlled architectures with high activity and durability is crucial for the future widespread adoption of PEMFC technology. Over the last years, nanostructured materials providing an alternative to carbon black have been investigated intensively with the objective of partially or totally replacing the carbon support [4]. This strategy was followed not only to improve the electrode durability, but also to benefit from the promotion of the oxygen reduction reaction (ORR) activity that the support may provide [5]. Metal oxides including SnO_2, TiO_x, Nb_2O_5, Ta_2O_5, WO_x, MoO_x, SiO_2 and Sb_2O_3 have been extensively studied due to their high corrosion resistance and electrocatalytic promoting effect [4,6,7]. Several strategies to modify their electronic structure *e.g.* doping with heteroatoms or preparing sub-oxides [8–10] have been employed to increase their electronic conductivity.

Transition metal nitrides [11–13] and carbides [14–16] present the required properties in terms of intrinsic electrical conductivity

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as well as chemical and mechanical stability to replace the carbon-based electrocatalyst supports conventionally used in PEMFC. Metal carbides can promote the electrocatalytic activity of Pt [17] and have also been investigated as non-noble ORR electrocatalysts in several media [18–21]. Because its electronic structure is similar to that of platinum, tungsten carbide was the earliest carbide to be assessed as an alternative electrocatalyst support [22]. Pt-catalysed WC micro- and nanomaterials showed enhanced electrocatalytic activity towards the ORR [23–25], as well as towards other reactions important for fuel cells and electrolysers (hydrogen oxidation, HOR [26], methanol oxidation reaction, MOR [27] and hydrogen evolution reaction, HER [28]). WC promoted the ORR activity of Fe/Co-based carbides in KOH, due to the synergistic effect of the three components [29]. Other metal carbides such as MoC [30,31], Mo_2C [32,33], TiC [12,34–37], and SiC [38] were investigated as electrocatalyst supports and high electrochemical surface area (ECSA) and ORR activity and improved corrosion resistance were reported. Few results are available with metal carbide supported platinum as the electrocatalyst in a single fuel cell.

Niobium carbide is of interest due to its high conductivity and stability, and yet has been little investigated as a fuel cell electrocatalyst support. Pt/NbC nanowires showed high electrochemical stability and higher MOR mass activity than conventional Pt/C [39]. The high electrical conductivity (*ca* 200 S cm^{-1}) of the catalyst was attributed both to its chemical composition and to the 1D nanostructured morphology, which decreases the boundary resistance between grains [39]. Indeed, a crucial role is played by the morphology of the support material that must provide high conductivity, surface area and appropriate porosity [40].

Nanomaterials with 1D morphology have been demonstrated to be promising supports with improved electron and gas transfer [41]. A simple, versatile and potentially scalable technique to prepare them is electrospinning, based on the formation of an electrified fluid jet [42]. So far, few examples of transition metal carbide nanofibres prepared by electrospinning have been reported with application in fuel cell electrodes. Pt deposited on electrospun TiC nanofibres with high surface area (500 m^2 g^{-1}) presented higher ECSA and ORR current density than platinum loaded carbon paper [43]. Non-catalysed WC@C nanofibres showed high stability and electrocatalytic activity towards the ORR [44].

We describe here the elaboration of an NbC/C nanostructure having a unique porous and hollow 1D morphology [45], and its use as a support for platinum nanoparticles synthesised with a microwave-assisted polyol method [46]. Pristine and catalysed materials were characterised for their morphology, crystal structure and chemical composition. The electrocatalytic activity, the electrochemical surface area and the stability of this novel electrocatalyst, in response to a voltage cycling accelerated stress test (AST) are described and compared to those of a commercial Pt/C electrocatalyst. Cathodes comprising Pt/NbC/C were developed and used in a membrane electrode assembly (MEA) and characterised in a single fuel cell.

2. Experimental section

2.1. Synthesis of NbC/C nanotubes

1.8 g of ammonium niobate oxalate (ANO) $(NH_4)_3[NbO(C_2O_4)_3]\cdot 2H_2O$ were dissolved in 5 g of distilled water and mixed with 4 g of ethanol containing 0.660 g of polyvinylpyrrolidone (PVP, Mw 1,300,000, Aldrich). ANO/PVP composite fibres were prepared by electrospinning this solution on a Spraybase setup at 15 kV, at a flow rate of 0.2 mL h^{-1} and at a needle-target distance of 10 cm (step 1). The collected fibres were calcined in air at 600 °C for 3 h to remove the carrier polymer (step 2) and to convert the precursor into Nb_2O_5. The resulting niobium oxide fibres were heated at 1100 °C in 10% CH_4/H_2 at a flow rate of 100 mL min^{-1} until their full conversion into NbC. This carburation step and the successive reactions taking place [47] were monitored with the thermal conductivity detector (TCD) signal of a Micromeritics ASAP 2010 Chemi System (step 3).

2.2. Characterisation of NbC/C nanotubes

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 ($\lambda = 1.541$ Å), and using a step size of 0.1° 2θ in the 2θ domain from 10 to 80°.

The fraction of residual elemental carbon in the niobium carbide nanotubes was derived from thermogravimetric analysis (TGA) using a Netzsch STA 409 PC apparatus.Elemental analysis for CHNS was carried out with an Elementar Vario Micro Cube apparatus.

The surface of the NbC/C nanotubes was characterised by X-ray photoelectron spectroscopy (XPS) using a Physical Electronics PHI 5700 spectrometer with non-monochromatic Mg K_α radiation (300 W, 15 kV, $h\nu = 1253.6$ eV) as excitation source. Spectra were recorded at a 45° take-off angle by a concentric hemispherical analyser operating in the constant pass energy mode at 25.9 eV, using a 720 μm diameter analysis area. Multipak 8.2b software was used for data analysis. A Shirley type background was subtracted from the signals. Recorded spectra were always fitted using Gauss-Lorentz curves. The accuracy of the binding energy (BE) values was within ±0.1 eV.

Nitrogen adsorption/desorption isotherms were determined at 77 K by means of a Micromeritics ASAP 2020 apparatus after outgassing overnight at 200 °C under vacuum ($<10^{-5}$ Torr). The specific surface area was calculated using the BET equation and taking 0.162 nm^2 as the cross-sectional area of one N_2 molecule. By using the Barrett-Joyner-Halenda (BJH) model, the pore volumes and pore size distributions were derived from the desorption branches of isotherms.

The electronic conductivity of NbC/C was determined at 25 °C from resistance measurements carried out using an in-house conductivity cell equipped with four gold electrodes and using the Van der Pauw calculation. Samples were analysed as flat pellets by pressing them at $3.4\ 10^8$ Pa for 10 min. In order to achieve a suitable cohesion of the pellet, 20 wt % of Nafion® (5 wt % dispersion Sigma-Aldrich) was added as a binder to the sample. The obtained mixture was dried in oven at 80 °C for 12 h.

2.3. Pt particles synthesis and deposition

A microwave-assisted polyol method was used to synthesise Pt nanocatalyst particles [46]. 70 mg of hexachloroplatinic acid (H_2PtCl_6. $6H_2O$, 99.9% Alfa Aesar) were dissolved in 50 mL of ethylene glycol (99.5%, Fluka) and the pH adjusted to 11 using 1 M NaOH solution (98%, Sigma Aldrich) in ethylene glycol. The resulting solution was heated at 120 °C for 6 min in a microwave reactor (MiniFlow 200SS Sairem). A suspension containing 40 mg of the nanotubes in 5 mL ethylene glycol was added to the Pt nanoparticle suspension and the pH was adjusted to 2. After gentle stirring for 24 h, the product was recovered by filtration, washed with milli-Q water and ethanol and dried overnight at 80 °C. The platinum loading was evaluated by X-ray fluorescence (XRF) using a Panalytical Axios Max spectrometer fitted with a 4 kW X-ray tube with