Effective debundling of carbon nanotubes and simultaneous synthesis of Pt nanoparticles by Nafion® induced emulsions

M. Soehn [a], S. Zils [a], N. Nicoloso [b], C. Roth [a,*]

[a] Institute for Materials Science, Renewable Energies group, TU Darmstadt, Petersenstr. 23, 64287 Darmstadt, Germany
[b] MAGNUM Fuel Cell AG, Haas-Str. 9, 64293 Darmstadt, Germany

ABSTRACT

Carbon nanostructures and, in particular, Single Wall Carbon Nanotubes (SWNT) or Multi Wall Carbon Nanotubes (MWNT) provide unique properties, notably outstanding chemical stability and electronic conductivity. Therefore they can be seen as a potential replacement for carbon black, which is frequently used as support material for polymer electrolyte membrane fuel cell (PEMFC) catalysts. This paper describes a new synthesis method to deposit platinum nanoparticles on carbon by using MWNT/Nafion® emulsions in the reduction reaction of hexachloroplatinate with ethylene glycol and butyl acetate. In contrast to other syntheses described in the literature, the formation of an emulsion allows effective debundling and a good dispersion of MWNTs in the solvent. This strategy helps to maintain a narrow Pt particle size distribution of $3\,nm \pm 0.5\,nm$ and a homogeneous dispersion of the nanoparticles on the support even at loadings of up to 50 wt%. It furthermore reduces agglomeration of the MWNTs during electrode manufacturing, so that an airbrush technique can be used, and enhances the ionic conductivity of the electrode layer. Catalyst morphology and distribution are investigated by transmission electron microscopy, X-ray diffraction and scanning electron microscopy. Electrodes are produced by a conventional airbrush technique on Nafion® membranes (Nafion® 117 and Nafion® NRE 212) and tested in a fuel cell test bench.

1. Introduction

Climate change and limited fossil fuel resources strongly push the development of more efficient energy conversion technologies e.g. the fuel cell technology, in which chemical energy is directly converted to electricity. Besides the high temperature fuel cells like SOFC and MCFC, which are used for small and mid range stationary combined heat and power plants, the low-temperature Polymer Electrolyte Membrane Fuel Cell (PEMFC) shows promising features for mobile and portable application. However, high cost and poor durability so far hinder their commercial market introduction, and therefore spark the interest in novel materials and innovative electrode preparation processes.

Carbon nanotubes, discovered by Iijima in 1991 [1], show unique properties regarding chemical stability, electronic conductivity [2] and tensile strength [3,4]. They also provide a high surface area of up to $2200\,m^2\,g^{-1}$ [5], which is essential for good catalytic efficiency. Without oxidative treatment hydrophobic surface properties can be observed. Depending on their morphology, carbon nanotubes (CNT) are separated into single wall (SWNT) and multi wall nan-

otubes (MWNT). Both types have a high aspect ratio with diameters of 1–20 nm and lengths of a few micrometers. Usually they form parallel bundles consisting of 2–50 tubes and can be prepared in ordered (aligned) [6] and disordered state (powders, networks) [7]. Many groups focus on carbon nanotubes as a replacement for the commercial carbon black as electrode substrate [8–11]. Carbon nanotubes have the disadvantage that they apparently offer less anchor sites for the deposition of metallic nanoparticles. Therefore, they require specific pre-treatments, as for example the addition of hydrophilic groups by acid treatment [12] or organic groups like diazonium salts [13]. However, probably due to their higher crystallinity they undergo less support corrosion in the extreme environment of PEM fuel cells.

A common way to deposit nanometer-sized catalyst particles with a narrow size distribution homogeneously on a high-surface area carbon support, e.g. Vulcan XC-72 or Ketjen black, is the reduction via ethylene glycol as described by Bock et al. [14]. This method is rather facile, reproducible and also cheap, as compared to e.g. chemical vapour deposition and the like. It is also suitable to deposit Pt on CNTs [15] [16], but unfortunately the 1-dimensional nature of the CNTs is prone to form aggregates and "nests" in ethylene glycol or other polar liquids [17]. These cannot easily be penetrated by the reactants. And thus, it proves difficult to obtain homogeneous nanoparticle dispersions on CNTs, especially at the high metal load-

* Corresponding author. Tel.: +49 0 6151 16 4391; fax: +49 0 6151 16 6023.
  E-mail address: c_roth@tu-darmstadt.de (C. Roth).

ings required for direct methanol fuel cells (DMFC) [9]. Usually, surfactants like sodium dodecyl sulfate [18] [19] or block copolymers [20] are used to mediate between polar liquids and CNTs. For fuel cell operation and also other catalytic reactions, these have to be removed prior to their application, as they might affect further reactions negatively. Moreover, surfactants seem to increase the contact resistances within a CNT buckypaper [21].

This paper presents a method to debundle and finely disperse CNTs in aqueous solution by using Nafion® ionomer and butyl acetate to form a stable emulsion. This helps to make a larger fraction of the CNTs accessible to the reducing agent, so that 3 nm Pt particles with a very narrow size distribution are homogeneously deposited on the support. In the same step, the CNTs are coated with Nafion® to improve their ionic conductivity. This appears to be also advantageous for the final electrode manufacturing step, since it allows applying the conventional airbrush technique also in those cases, in which CNTs are used as support material.

2. Experimental

2.1. Sample synthesis

60 mg multi wall carbon nanotubes (Elicarb© from Thomas Swan, U.K.) are mixed and stirred with 60 mL nitric acid (68%) and treated with ultrasound (Hielscher UPV 100) for 10 min to remove metallic impurities. After diluting with water, the suspension is vacuum-filtrated over a 47 mm polycarbonate membrane with 0.4 μm pore size. Remaining acid is removed by rinsing with water several times. The wet CNT residue is removed from the polycarbonate membrane and mixed with 60 mL butyl acetate while stirring and ultrasonic treatment for 10 min, leading to a homogeneous dispersion. For the platinum precursor solution, 145 mg potassium hexachloroplatinate (Sigma–Aldrich) is dissolved in 10 mL ultra pure water at 50 °C. 60 mL ethylene-glycol and the platinum precursor solution are mixed with the MWNT-butylacetate dispersion in a 250 mL round bottom flask. After adding 0.5 mL of 5% Nafion® solution (Dupont D521) and another 15 min of ultrasonic treatment and stirring, the two phase boundary between the liquids disappears and a homogeneous milky-grey emulsion is created.

The emulsion is heated in an oil bath from room temperature to 170 °C and the mixture is held for 120 min under reflux conditions while stirring. Samples are taken during the synthesis for a detailed investigation by XRD. After cooling down, the catalyst-solvent mixture is filtered over a polycarbonate filter. Rinsing with 1:1 isopropanol–water removes the remaining ethylene glycol and butyl acetate. After removal of the filter, the wet residue is mixed with 30 mL isopropanol and 30 mL water by ultrasonic treatment to create a sprayable ink. Nafion® and/or PTFE solution can be added here.

2.2. Sample characterization by XRD, TEM, SEM and TGA-MS

For X-ray diffraction (XRD) measurements, samples (<1 mL) are taken from the liquid phase during the synthesis repeatedly. The fluid is dropped slowly onto a polycarbonate filter and a mild vacuum is applied. After drying, the polycarbonate membrane is mounted in an XRD sample holder and measured in a STOE STADI P in transmission geometry with Ge-monochromized Cu-Kα radiation and a position-sensitive detector with a 40° aperture. Average particle sizes are estimated by Rietveld refinement using the FULL-PROF suite [22]. Transmission electron microscopy (TEM) samples are prepared by dispersing a few micro litres of catalyst ink in methanol and letting 1 drop of this mixture dry on a copper TEM grid. Subsequently, a JEOL JEM 3010 with LaB$_6$ cathode and an acceleration voltage of 300 kV is used for examination. Scanning electron

microscopy (SEM) images are recorded by cutting the sample with a razor blade and mounting the pieces on a SEM sample holder to determine the electrode thickness. Secondary electron (SE) images are recorded with a FEI Quanta 200 FEG. For the thermogravimetric analysis (TGA-MS) a fragment of the as prepared MWNT-Pt filter substrate (61.4 mg MWNTs, 147.5 mg K$_2$PtCl$_6$, 0.5 mL Nafion® solution) is dried in air at 120 °C for 24 h and heated under a flow of 25 mL min^{-1} O$_2$ and 10 mL min^{-1} Ar to 1000 °C using a Netzsch STA 429. Residual gases are analysed by mass spectrometry.

2.3. MEA preparation and electrochemical investigation by IV curves

For membrane preconditioning, 5 × 5 cm pieces of Nafion® 117 are heated up to 80 °C in 500 mL of 1 M sulphuric acid with 20 mL of 30% hydrogen peroxide solution for 2 h. After rinsing with DE-water, the membrane is fixed to a heated table (110 °C) by means of a mild vacuum. Airbrush is used to apply the aqueous catalyst ink onto the membrane, which is covered by a mask to form a round centred area (Ø = 37 mm). 2 mL ink is sprayed on each side, which corresponds to a maximum Pt loading of 0.2 mg cm^{-2}. The given loadings correspond to the upper limit, because it is difficult to determine the amount of overspray (estimated: 10–20%). Each layer is allowed to dry before it is covered by the next one. The MEA is covered with two pieces of carbon cloth (Elat© LT1400, with micro porous layer, by Etek Inc.) and fixed between gold-plated stainless steel plates with a meander flow field. The cell is fed with pure H$_2$ and O$_2$ at atmospheric pressure. Both gases are humidified by bubblers at 90 °C. The cell temperature is set to 75 °C. After a couple of hours in cell conditioning, IV curves are recorded in potentiostatic mode with an electronic load, compensating contact resistances. Gas flows are adjusted in such a way that reaction products are removed even at highest currents (stoichiometry >1).

3. Results and discussion

3.1. Deposition of noble metals

It is commonly observed that CNTs form aggregates and "nests", when added into polar solvents for the deposition of nanoparticles. A mixture of CNTs and butyl acetate, however, leads to a homogeneous black dispersion, which is stable for days after ultrasonic treatment. Adding ethylene glycol and yellow-coloured aqueous K$_2$PtCl$_6$ solution, a sharp phase boundary is observed in Fig. 1. Even with strong ultrasonic treatment it is not possible to mix the phases. If some Nafion® solution is added, a stable grey emulsion can be created by ultrasonic treatment. It seems that Nafion® acts as a surfactant. Microscopic analysis shows spheres (diameter of ~50 μm) with a black shell in clear liquid (Fig. 2).

To distinguish ethylene glycol and butyl acetate, fluorescin (CAS: 2321-07-5) is used as colouring agent. Without the black MWNTs, it can be clearly seen in Fig. 3 that the colourless butyl acetate is located inside the spheres, whereas the ethylene glycol phase remains outside. This effect can be explained by the amphiphilic nature of Nafion® with its hydrophobic tetrafluoroethylene backbone and hydrophilic SO$_3^-$ groups. A Critical Micelle Concentration (CMC) could not be detected with diluting experiments with the Nafion® solution. Therefore, the influence of other surfactants could be excluded. For the observed effects we assume a model as depicted in Fig. 4: Nafion® forms the boundary between ethylene glycol and butyl acetate. The CNTs tend to move towards the hydrophobic backbone of the Nafion® molecules, whereas the hygroscopic SO$_3^-$ groups become oriented towards the ethylene glycol phase. This leads to a high interface area of approx. 12 m^2 for this 120 mL batch, and provides an excellent debundling of