Carbon nanotubes and other nanostructures as support material for nanoparticulate noble-metal catalysts in fuel cells

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For polymer electrolyte membrane fuel cells (PEMFC) using hydrogen as fuel and operating at low temperature (60-80°C) the most efficient catalysts for the hydrogen oxidation reaction (ORR) are platinum alloys. Similarly, at the air side of the fuel cell, platinum is the most efficient catalyst for the oxygen reduction reaction (ORR). To reduce the cost of the noble metal catalyst, through maintaining a high catalytic activity towards the HOR and ORR, small metal nanoparticles in the size range 1.5 nm are deposited or grown onto an electrocatalyst and inert support material.[1-2] The support material preferred due to its anchoring abilities is Vulcan XC-72 carbon black. Suitable electrochemical surface area (ESA) is obtained with platinum loadings of approximately 20 wt.%, for platinum supported by Vulcan XC-72 carbon black.[3]

At fuel cell operation the catalyst particles are subjected to very harsh conditions, such as low pH, high potential drop and a warm and humid environment, which is needed for the proton-conducting membrane to operate.

Electrode preparation and dispersion properties

The preparation of the RDE and RRDE working electrodes, used for characterisation of fuel cell catalysts, is performed by preparation of a dispersion/ink, pipetting the desired amount and applying it to the electrode disc surface. Upon drying in inert atmosphere, a drop of Nafion® dispersion is applied and dried in order to form a ~0.2 µm thick porous Nafion® layer (figure 4). [10] This electrode preparation method is very easily applicable with carbon blacks and carbon-black-supported catalyst. When this technique is employed on carbon nanostructured supports, the van der Waals attractive forces cause the support to agglomerate and form islands on the electrode surface. To be able to evaluate ORR effects properly the preparation of well dispersed catalyst on the electrode surfaces is needed, which presently proposes great challenges.

Defect characterisation of carbon substrates

Electron spin resonance (ESR) spectroscopy relates the carbon signal to the ratio between localised spins at structural irregularities and conductive carriers associated with electronic conduction bands between graphene layers (figure 1). The measurements were performed with annealed (800°C) magnesium oxide as internal reference and diluting material. Raman spectroscopy and X-ray photon spectroscopy (XPS) are surface sensitive spectroscopy methods used for CNT defect evaluation and carbon species determination (figure 2). [6-9]

Peroxide formation

For fuel cells the transient species investigated is hydrogen peroxide (H₂O₂) formed during the ORR. Hydrogen peroxide breaks chemically down into hydroxyl radicals (OH•), which may cause membrane degradation and carbon corrosion.

To evaluate the species produced during cell operation, the RRDE can be used to measure transient species formed during the potential sweep (figure 3). The catalyst aging and subsequent loss of efficiency are among other things due to the platinum nanoparticles agglomerating on the support material and corrosion of the carbon support material. As alternative to carbon black, nanostructures of carbon are being investigated for their use as support material for platinum and platinum-alloy nanoparticles. The highly ordered surface structure of carbon nanofibers (CNF) [4], carbon nanotubes (CNT) [5] and other nanostructured carbon materials give them high stability towards carbon corrosion, while the substructure layers provide good electron-conductive properties. As the ordered surface structures provide resistance towards carbon corrosion, it is inadvertently equally more difficult to functionalize the carbon nanostructures with metal nanoparticles and to prepare catalysts without the use of auxiliary chemicals. This also affects the characterisation methods needed to compare these materials.

Differences in Raman spectra signals obtained from Swanepoel CNF (SD-CN) and unmodified Swanepoel CNFs (A) and (C) show the first derivative ESR carbon signal for unmodified SD-CN compared to acid treated fibres. On the left the fibres were treated in conc. sulfuric acid (G002) and 4M H₂SO₄/0.1M HMS (G004) for 2h at 80°C. On the right the fibres were treated in 0.1M HNO₃ (G005), 0.1M HNO₃/0.01M HMS (G006) and 4M H₂SO₄/0.1M HMS (G008) for 4h at 120°C. Most of the samples exhibit no noticeable change observed, except G005-G007, for which the electron conducting signal electrons, and G006-G007, for which it increases.

Figure 1: (A) show the first derivative ESR carbon signal of acid treated Swanepoel CNF (G002), untreated Swanepoel CNF (SD-CN) and an unmodified Swanepoel CNF sample (SW-CN). (B) show the first derivative ESR carbon signal for unmodified SD-CN compared to acid treated fibres. On the left the fibres were treated in conc. sulfuric acid (G002) and 4M H₂SO₄/0.1M HMS (G004). (C) show the first derivative of the ESR carbon signal for unmodified SD-CN compared to acid treated fibres. On the left the fibres were treated in conc. sulfuric acid (G002) and 4M H₂SO₄/0.1M HMS (G004). (D) shows the first derivative of the ESR carbon signal for unmodified SD-CN compared to acid treated fibres. On the left the fibres were treated in conc. sulfuric acid (G002) and 4M H₂SO₄/0.1M HMS (G004). (E) shows the first derivative of the ESR carbon signal for unmodified SD-CN compared to acid treated fibres. On the left the fibres were treated in conc. sulfuric acid (G002) and 4M H₂SO₄/0.1M HMS (G004). (F) shows the first derivative of the ESR carbon signal for unmodified SD-CN compared to acid treated fibres. On the left the fibres were treated in conc. sulfuric acid (G002) and 4M H₂SO₄/0.1M HMS (G004).

Figure 2: Differences in Raman spectroscopy signals obtained from Swanepoel CNF (SD-CN), unmodified carbon nanotubes (CNT) and different types of carbon blacks (Vulcan and Acetylene blacks) can be seen (A). The defect induced D-band (amorphous carbon) and G-band (graphite) intensities ratios vs. the respective G-band intensities are shown at the top graph of (B). The lower graph at (B) shows the atomic oxygen content (%O) determined from XPS and the oxygen containing species evaluated by Gaussian peak fitting of the C 1s signal (example for SD-CN shown at (C)). The peak fits are restricted and normalised with the total peak area and oxygen content.

Figure 3: (A) shows the XPS scan of the ring and disc of an RDE for the positive (A) and (C) sweep with different carbon support materials attached to the glassy carbon disc electrode in 0.5 M HClO₄. (A1). The measurements are made in 0.5 M HClO₄ saturated electrolyte. The current response from Ar saturated 0.5 M HClO₄ (A) shows that the electrode has been suberated. (B) shows the amount of hydrogen peroxide generated on the carbon support is calculated from the Faraday current responses at the electrode ring. The coulometric integration is excepted to 2.2 V vs. NH₄ClO₄. The signal of 0.22 V in (A) shows the D-band of the EDX chart.

Figure 4: RDEs prepared by a two-step drop coating of catalyst and Nafion®.[6] shows that the carbon black supported platinum catalyst is well dispersed on the electrode surface. (B) shows that the CNF/CNT-based catalysts agglomerate after application onto the glassy carbon electrode. (C) shows the same CNF/CNT-based catalyst with PVP as dispersing agent.

To disperse the different carbon nanostructured supports and supported materials different auxiliary agents such as solvents, dispersing agents and nanohalides can be used (figure 5).

Figure 5: Graphite discs, used to emulate glassy carbon disc electrodes. On these discs a drop of gCNF dispersed by different auxiliary agents has been put and dried. In (B) the dispersion was made in pure 3-propanol, in (C) the graphitic CNF were dispersed in a 1:3 mixture of 2-propanol and water and in (C) the dispersion was made in water using polyvinyl pyrrolidone (PVP) (10%) as dispersing agent. The light areas are CNF, whereas the darker areas are the graphite disc substrate.

Figure 6: (B) Koutecky-Levich plots of ORR in 0.1 M HClO₄ for different Pt/CNFn catalysts at 0.9 V vs. RHE and Pt/Vulcan (BASF). The CNF samples are dispersed using PVP 0.5 w.-% ratio PVP/C. (A) shows anodic ORR polarization curves for a Pt/CNFn catalyst dispersed under different conditions in 0.1 M HClO₄, (aq) electrolyte. The current responses from Ar have been subtracted.

Figure 7: Differences in Raman spectroscopy signals obtained from Swanepoel CNF (SD-CN), unmodified carbon nanotubes (CNT) and different types of carbon blacks (Vulcan and Acetylene blacks) can be seen (A). The defect induced D-band (amorphous carbon) and G-band (graphite) intensities ratios vs. the respective G-band intensities are shown at the top graph of (B). The lower graph at (B) shows the atomic oxygen content (%O) determined from XPS and the oxygen containing species evaluated by Gaussian peak fitting of the C 1s signal (example for SD-CN shown at (C)). The peak fits are restricted and normalised with the total peak area and oxygen content.

Figure 8: (B) Koutecky-Levich plots of ORR in 0.1 M HClO₄ for different Pt/CNFn catalysts at 0.9 V vs. RHE and Pt/Vulcan (BASF). The CNF samples are dispersed using PVP 0.5 w.-% ratio PVP/C. (A) shows anodic ORR polarization curves for a Pt/CNFn catalyst dispersed under different conditions in 0.1 M HClO₄, (aq) electrolyte. The current responses from Ar have been subtracted.