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

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Publication date:
2011

Document version
Peer reviewed version

Citation for published version (APA):

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Download date: 19. jan., 2019
For polymer electrolyte membrane fuel cells (PEMFC) using hydrogen as fuel and operating at low temperature (60-100°C) the most efficient catalysts for the hydrogen oxidation reaction (HOR) 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 onto or grown onto an electrode-conducting 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 catalysts 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, jetting 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.

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).

OHR kinetic properties have been investigated by using PVP for dispersion (figure 6).

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 subsurface 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.

Defect characterisation of carbon substrates
Electron spin resonance (ESR) spectroscopy relates the carbon signal ratio between localised spins at structural irregularities and conductive carriers associated with electron 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 spectroscopic methods used for CNT detection 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 catalytic reaction 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 subsurface 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.

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