



# Oxygen reduction reaction activity and long-term stability of platinum nanoparticles supported on titania and titania-carbon nanotube composites

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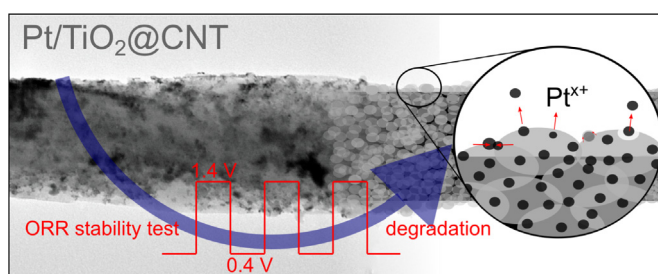
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## HIGHLIGHTS

- Synthesis of TiO<sub>2</sub> covered CNTs as conductive support for Pt based ORR catalysts.
- Pt/TiO<sub>2</sub>@CNT catalysts show an ORR activity comparable to commercial Pt/C (E-Tek).
- TiO<sub>2</sub> support stabilizes Pt NPs against particle growth and Pt dissolution.
- Under start-stop conditions TiO<sub>2</sub> supported catalysts show high loss of ORR activity.
- Partial overgrowth of the Pt NPs by a TiO<sub>2</sub> layer during start-stop stability tests.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Aiming at Pt nanoparticle catalysts for application in polymer electrolyte membrane fuel cell (PEMFC) cathodes, which are highly active and more corrosion resistant under realistic mobile applications than common Pt/C catalysts, we have prepared and investigated Pt catalysts supported on highly stable, nanostructured composite materials containing carbon nanotubes (CNTs) and titania. TiO<sub>2</sub>@CNT composite materials are synthesized via sol-gel processing and subsequent Pt deposition. The physical and electrochemical properties as well as the stability of these catalysts, as determined by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), rotating ring disk electrode (RRDE) measurements and accelerated degradation tests (ADTs), were compared with those of commercial Pt/C, Pt/TiO<sub>2</sub> and Pt/CNT. The measurements reveal a high activity of the composite catalyst, comparable to that of the Pt/C catalyst, but an almost complete loss of ORR activity upon an ADT procedure simulating start-stop behavior. In contrast to carbon supported catalysts, where degradation is mainly associated with corrosion at high potentials, we find the titania supported catalysts to mainly suffer from the reductive treatment in the ADTs. Consequences for the use of Pt catalysts supported on reducible oxides such as TiO<sub>2</sub> as cathode catalysts in fuel cell applications are discussed.

## 1. Introduction

The lifetime of fuel cells, which is largely related to the durability of the catalyst, is a crucial factor for their successful commercialization in

stationary and automotive applications. This has stimulated intense research of degradation effects in fuel cells and the development of new approaches to improve the cathode catalyst stability [1–11]. Main challenge is to maintain the activity for the oxygen reduction reaction

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(ORR) also under conditions relevant for practical operation of polymer electrolyte membrane fuel cells (PEMFCs) [1]. It has been shown that several factors can reduce the lifetime of PEMFC catalysts, including (1) platinum particle dissolution and sintering [3,12], (2) dissolution of the non-noble element in bimetallic PtMe (Me = 2nd metal) catalyst particles [13,14], or (3) corrosion of the carbon support under cathode operation potentials and the resulting detachment of the Pt nanoparticles [3,12,15,16]. Therefore, different groups including ours started to explore possibilities to replace the commonly used high surface area carbon supports such as Vulcan XC-72 by more corrosion resistant materials [4,8,17–19]. It was demonstrated, e.g., that novel nanostructured carbon materials such as carbon nanotubes and other carbon modifications with mostly graphitic structures are more corrosion resistant under oxidizing conditions than conventional carbon supports [1,20]. The graphitic surfaces of these materials contain fewer defect sites than high surface area carbons, thereby reducing the sensitivity towards oxidation. Nevertheless, also graphitized carbon supports cannot fully prevent carbon corrosion.

Several groups claimed that titania based support materials can improve the stability of Pt catalysts, with only low ORR activity losses compared to Pt/C [4,18,21]. In most studies, however, the low electric conductivity of the catalysts, which leads to increased Ohmic losses, was improved by either doping TiO<sub>2</sub>, e.g., with nitrogen or carbon [19,21], by addition of conductive materials such as carbon [17,22,23], or by using very thin TiO<sub>2</sub> films on a conducting substrate [23–25]. In order to limit losses in stability due to the incorporation of oxidizable carbon materials, a number of groups used highly corrosion resistant multi-walled carbon nanotubes (MWCNTs). This conductive backbone gives, in combination with oxide materials such as TiO<sub>2</sub>, a so-called composite Pt catalyst for the ORR [10,23,26,27]. It turned out, however, that also these catalysts can suffer from lower activities due to high electric resistance, introduced by a too thick titania layer [10,27]. In addition, the CNTs had to be surface functionalized, e.g., by treatment in acid, to deposit titania on them, which increased their susceptibility towards corrosion again.

Here we report results of a study where, following up on this idea, we pursued a different synthetic approach, depositing a thin layer of titania on well-conducting and corrosion resistant MWCNTs via a modified sol-gel process [28–30]. Using benzyl alcohol as a linker between the hydrophobic CNT surface and the hydrophilic titania precursor, this results in a rather homogeneous formation of the TiO<sub>2</sub> layer on top of the MWCNTs, with a well-controllable titania layer thickness. The layer thickness can be adjusted rather accurately by the amount of water added to the reaction mixture during the sol-gel synthesis. Since this deposition procedure does not require any surface functionalization, we expect to maintain the higher corrosion stability of the CNTs compared to that of standard carbon supports. The corrosion stability of the CNTs should be further improved by the fact that the Pt particles (diameter of 2.5–3 nm) are preferably deposited on the titania layer, since the non-surface-functionalized CNT surface lacks defect sites, where the Pt particles can attach to during the polyol process [31]. Considering that the carbon corrosion is catalyzed by Pt nanoparticles in contact with the carbon surface [16,32], and that the Pt particles are not in direct contact with carbon, this should further reduce carbon corrosion.

Following a brief description of the instrumentation and the experimental procedures in section 2, including the catalyst preparation, we will first present results of the structural and electronic characterization of the nanostructured Pt/TiO<sub>2</sub>@CNT composite catalysts and, for comparison, of a commercial Pt/C catalyst, a Pt/TiO<sub>2</sub> catalyst, and a Pt/CNT catalyst. The chemical properties of these catalysts were characterized by differential electrochemical mass spectrometry (DEMS) (section 3.2) and the ORR performance, including the activity and the selectivity for the 4-electron reduction to water, was evaluated by rotating ring disk electrode (RRDE) measurements (section 3.3). Finally, we evaluated the stability of these catalysts in accelerated degradation

tests (ADTs), simulating start-stop conditions, which were also performed in the RRDE setup [1,7,33–37]. The main conclusions from these findings are summarized in section 4.

## 2. Experimental

### 2.1. Catalyst synthesis

For the synthesis of the CNT-based catalysts (Pt/CNT and Pt/TiO<sub>2</sub>@CNT), first, a cleaning process was performed to remove possible metal impurities [38]. For the Pt/CNT catalyst, the cleaned CNTs were surface functionalized by acidic treatment before Pt deposition [38]. The carbon free TiO<sub>2</sub> support was synthesized using an adjusted sol-gel process [39]. Similarly, the TiO<sub>2</sub>@CNT composite support was synthesized via a sol-gel process approach employing benzyl alcohol as a complexing agent, as suggested by Eder et al. [28–30]. On all support materials (CNT, TiO<sub>2</sub> and TiO<sub>2</sub>@CNT), platinum nanoparticles were deposited via a polyol process [31]. The exact Pt loading of the catalysts was determined by inductively coupled plasma optical emission spectrometry (ICP OES, Horiba Ultima 2).

The detailed description of the synthesis and the used materials is presented in the supporting information (chapter 1.1).

### 2.2. Physical characterization

The bright-field transmission electron microscopy (BF-TEM) measurements were performed with a Jeol JEM-1400 instrument, using electron energies of up to 120 kV. Samples were prepared by depositing 0.05 mL of a dilute catalyst suspension in ethanol ( $< 1 \text{ mg mL}^{-1}$ ) on a Cu-supported carbon grid (Cu-grid, Plano, 300 mesh). The Pt particle size distribution was determined by evaluating the diameters of  $> 300$  individual Pt particles. For the Pt/CNT, which does not show separated particles on the smooth CNT surfaces, the particle size was obtained by measuring the particles at the ends of the CNTs, where they are well separated. However, the Pt particle size results for Pt/CNT do not represent the Pt structures shown in Fig. 1b and f.

Energy-dispersive X-ray Spectrometry (EDX) was performed with a Zeiss Leo 1550 instrument using an Oxford Instruments EDX sensor and the INCA Suite 4.09 software for evaluation. For sample preparation, catalyst films were deposited on a silicon wafer by pipetting the catalyst suspension on the silicon wafer and drying in a N<sub>2</sub> atmosphere.

The surface area of the synthesized support materials were determined by N<sub>2</sub> sorption measurements, using a Micromeritics ASAP 2420 instrument and a temperature of  $-196 \text{ }^\circ\text{C}$  in a relative pressure range of  $p/p_0$  between  $4 \times 10^{-6}$  and 0.99. The single point Brunauer, Emmett, and Teller (BET) method was applied at  $p/p_0 = 0.211$  for calculation of the BET surface area. Additionally, the surface area was calculated using the Barrett, Joyner and Halenda (BJH) method (adsorption cumulative surface area). For high-resolution transmission electron microscopy (HR-TEM), a FEI Titan 80–300 was used with an acceleration voltage of 300 kV. X-ray diffraction (XRD) measurements were performed using a Bruker D8 Advance instrument (Bruker Karlsruhe), applying Cu-K $\alpha$  radiation ( $\lambda = 0.154 \text{ nm}$ ) in a  $2\theta$  range of  $5^\circ$ – $80^\circ$  ( $0.02^\circ$  continuous mode, 0.5 s per step).

X-ray photoelectron spectroscopy (XPS) measurements were performed using a Physical Electronics PHI 5800 Multi ESCA System, applying monochromatic Al K $\alpha$  radiation, at an electron emission angle of  $45^\circ$  and a pass energy of 29.35 eV for detail spectra. The samples were prepared by depositing and drying 20  $\mu\text{L}$  of an aqueous catalyst suspension on a silicon wafer, which was pre-treated in ultrapure water (MilliQ), KOH<sub>aq.</sub> and H<sub>2</sub>SO<sub>4conc.</sub> CasaXPS software was used to deconvolute the measured signals, employing a Shirley background correction. In order to correctly reflect the measured, asymmetric Pt(4f) signals, the Gaussian/Lorentzian sum form (SGL) was modified by an exponential asymmetric tail (T). The parameters were selected to optimize the fit of the Pt(4f) peak on the reference Pt/C catalyst, resulting

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