



Short communication

## Pd deposited on functionalized carbon nanotubes for the electrooxidation of ethanol in alkaline media



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### ABSTRACT

Large scale commercialization of direct ethanol fuel cells is hampered by the high cost and scarcity of noble metal electrocatalysts employed at both the anode and cathode. We demonstrate improved utilization of palladium as anode catalyst for ethanol oxidation by exploiting the strong interaction between Pd nanoparticles and nitrogen-doped carbon nanotubes (NCNTs) as support. 0.85 wt% Pd supported on NCNTs achieved a specific current density of  $517 \text{ A g}_{\text{Pd}}^{-1}$  compared with  $421 \text{ A g}_{\text{Pd}}^{-1}$  for 0.86 wt% Pd on oxygen-functionalized carbon nanotubes. The electrocatalytic performance deteriorated only gradually and catalysis was sustained for at least 80 h.

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## 1. Introduction

Carbon-based materials comprising activated carbon [1–3], network-like carbon nanofibers [4], graphene sheets [5], carbon spheres (CS) [3,6,7], and carbon nanotubes (CNTs) [3,8–11] have attracted considerable attention as supports in electrocatalysis. The unique properties of CNTs such as their high surface area, chemical stability as well as electric conductivity make them attractive for electrocatalytic applications. Further, the open three-dimensional network structure of CNTs minimizes mass transport limitations mimicking the inverse structure of conventional porous metal oxide catalysts commonly applied in heterogeneous catalysis [12]. In addition, the structural modification of carbon materials by incorporation of heteroatoms positively influences their conductivity and hydrophilicity [11], and in some cases their electrocatalytic properties [13]. The heteroatoms may serve as nucleation and anchoring sites for metal nanoparticles (NPs) leading to increased activity and stability [7,14,15].

The electrooxidation of alcohols, for example in direct alkaline alcohol fuel cells, is efficiently catalyzed by Pt present as supported alloy (PtSn [16], PtRu [10]), mixed with oxides (CeO<sub>2</sub>, NiO [17]) or as Pt nanoparticles on a high surface area support [3,16]. However, Pt-based catalysts are very costly, which makes them unappealing for large-scale applications. Pd as lower homologue of the Pt group metals also shows excellent catalytic activity and is even reported to outperform Pt in some cases [1,3]. Pd on nitrogen-doped CS (NCS) [6], Pd on CNTs

grown on carbon fiber paper [18], Pd on carbon nanofibers [4] and Pd on surface-functionalized CNTs [19] are highly active catalysts in the electrooxidation of ethanol (EtOH) in alkaline media. Nitrogen-doped carbon nanotubes (NCNTs) show much better properties as catalyst support due to the strong interaction between metal nanoparticles and NCNTs [20–22], and they are also potent electrocatalysts for some reactions [23,24]. However, to the best of our knowledge, there are no studies available focusing on the electrooxidation of EtOH by Pd nanoparticles supported on NCNTs (Pd/NCNT) and on oxygen-functionalized carbon nanotubes (Pd/OCNT).

Pd/NCNT and Pd/OCNT were recently found to be extraordinarily active in hydrogenation reactions [15]. We report the application of Pd/NCNT and Pd/OCNT as electrocatalysts in the ethanol oxidation reaction (EOR) in NaOH (1 M). Pd/NCNTs exhibited very high electrocatalytic activity, specific current densities, and stability as compared with Pd/OCNT for EtOH oxidation at relatively low Pd loadings of 0.85 wt% and 0.86 wt%, respectively.

## 2. Experimental

### 2.1. Materials

The catalysts were synthesized following the procedure described in ref. [15]. In brief, commercially available CNTs (Baytubes® C 150 P) were purified using dilute HNO<sub>3</sub> solution (1.5 M) and treated with HNO<sub>3</sub> vapor at 473 K for 48 h to obtain OCNTs. Further treatment of the OCNTs with 10 vol% NH<sub>3</sub> in He at 673 K for 6 h yielded NCNTs. Pd nanoparticles were deposited by a colloidal deposition method

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decoupling particle formation from the deposition on the support. For this, NCNTs or OCNTs were exposed to dissolved  $\text{Pd}(\text{OAc})_2$  in anhydrous methanol under stirring for 10 min. After removal of the solvent, the materials were dried at 333 K for 12 h, heated to 473 K in He, reduced in 10 vol%  $\text{H}_2/\text{He}$  ( $100 \text{ mL min}^{-1}$ ) for 2 h, and finally cooled to room temperature in He.

## 2.2. Preparation of electrodes

Glassy carbon (GC) rotating disc electrodes (RDEs) (3.8 mm diameter) were polished to a mirror finish using  $0.05 \mu\text{m}$   $\text{Al}_2\text{O}_3$  suspensions before each measurement. Catalyst inks ( $5 \text{ mg mL}^{-1}$ ) were prepared using a mixture of 49/49/2 vol% of  $\text{H}_2\text{O}/\text{EtOH}/\text{Nafion}^{\text{®}}117$ . This mixture was ultrasonically treated for 1 h before  $5.0 \mu\text{L}$  of the ink was drop-coated on the electrodes ( $0.11 \text{ cm}^2$ ), which were stored overnight under atmospheric conditions to obtain a dried catalyst layer.

## 2.3. Electrochemical characterization

All electrochemical measurements were performed in a three-electrode electrochemical cell using the catalyst-modified rotating disk electrode (RDE) as working electrode (WE), a Pt mesh as counter electrode (CE), and a  $\text{Ag}/\text{AgCl}/3 \text{ M KCl}$  electrode as reference electrode (RE). Electrochemical experiments were controlled by a Metrohm-Autolab potentiostat/galvanostat. All applied potentials were recorded vs. the  $\text{Ag}/\text{AgCl}/3 \text{ M KCl}$  RE and converted to the reversible hydrogen electrode (RHE) scale.  $\text{O}_2$ -free conditions were obtained by purging of the electrolyte with Ar. Each WE was electrochemically conditioned in 1 M NaOH by applying continuous cyclic voltammograms at a scan rate of  $50 \text{ mV s}^{-1}$  until reproducible voltammograms were attained. The EOR was investigated by cyclic voltammetry (CV) in 1 M NaOH containing 1 M EtOH at a scan rate of  $10 \text{ mV s}^{-1}$  with the electrode either stationary or at rotation rates of 1600 rpm. The experiments were performed multiple times to identify erroneous measurements. Stability was investigated chronoamperometrically at a constant potential ( $0.92 \text{ V}$ ) and 400 rpm of electrode rotation.

## 3. Results and discussion

NCNTs and OCNTs were loaded with small amounts of Pd nanoparticles to exploit the synergetic interaction between Pd and the carbon support simultaneously enhancing the activity of Pd towards EtOH oxidation and improving its utilization. The loading of Pd on the supports after the synthesis was confirmed by elemental analysis with ICP-OES to be 0.85 wt% for Pd/NCNT and 0.86 wt% for Pd/OCNT. STEM images of the samples reduced at  $200 \text{ }^\circ\text{C}$  in  $\text{H}_2$  as reported earlier [15] revealed the typical tubular CNT morphology and well dispersed Pd nanoparticles over the outer surface of the CNTs with essentially equal average particle sizes of  $2.7 \pm 0.5 \text{ nm}$  for Pd/NCNT and  $2.7 \pm 0.8 \text{ nm}$  for Pd/OCNT. In the same study XPS experiments revealed a strong interaction between Pd nanoparticles and N-doped CNTs, which was not identified for Pd nanoparticles on OCNTs [15]. The mass-related Pd surface areas of both catalysts were derived from  $\text{H}_2$  chemisorption as  $82.4 \text{ m}^2 \text{ g}^{-1}_{\text{Pd}}$  for Pd/NCNT and  $51.2 \text{ m}^2 \text{ g}^{-1}_{\text{Pd}}$  for Pd/OCNT, which is in agreement with a broader particle size distribution of Pd/OCNT compared with Pd/NCNT [15]. The electrochemically active surface areas (ECSA) of the catalysts were determined by integrating the PdO reduction peak of CVs at a scan rate of  $50 \text{ mV s}^{-1}$  under oxygen-free conditions and assuming a PdO monolayer reduction charge of  $405 \mu\text{C cm}^{-2}$  [5,25,26]. The obtained values of  $41.1 \text{ m}^2 \text{ g}^{-1}_{\text{Pd}}$  and  $37.4 \text{ m}^2 \text{ g}^{-1}_{\text{Pd}}$  for Pd/NCNT and Pd/OCNT, respectively, are in good agreement with the TEM and  $\text{H}_2$  chemisorption results as well as with the theoretical Pd surface area of approximately  $83.2 \text{ m}^2 \text{ g}^{-1}_{\text{Pd}}$  assuming hemispherical 3 nm particles [27]. The discrepancy between the chemisorption and ECSA values can be ascribed to the different conditions used in the experiment. Immersed in the electrolyte, only the Pd particles in contact

with the electrolyte are addressable, whereas chemisorption of gas-phase molecules allows access to a greater fraction of the available Pd nanoparticles. The analysis of the chemisorption data requires the extrapolation to monolayer capacity and a stoichiometry of Pd/H of 1/1, whereas the ECSA is based on the assumption that a monolayer of PdO is generated during the anodic scan. Taking the underlying assumptions of these two methods into account, the ECSAs determined for Pd/NCNT and Pd/OCNT are considered reasonable.

The activities of Pd/NCNTs and Pd/OCNTs towards EtOH oxidation were investigated by CV and the results are presented in Fig. 1a and b, respectively. The CVs show similar features with two well pronounced oxidation signals. The peak current densities as well as specific current densities for the two catalysts are shown in Fig. 2a. The oxidation wave in the forward scan (p1) is assigned to EtOH. With increasing potential,  $\text{OH}^-$  groups as well as EtOH species are adsorbed on the catalyst and EtOH is readily oxidized. To investigate whether the decline in the electrocatalytic EtOH oxidation currents was due to diffusion limitation, the electrodes were rotated at 1600 rpm. If the decline in the intensity of p1 was due to limited diffusion of EtOH to the electrode, then an increase in the peak current with electrode rotation would be expected. However, the peak current decreased with increasing rotation suggesting a surface-confined process such as active site poisoning by the incomplete oxidation of intermediates and products such as  $\text{CHO}_{\text{ads}}$  or

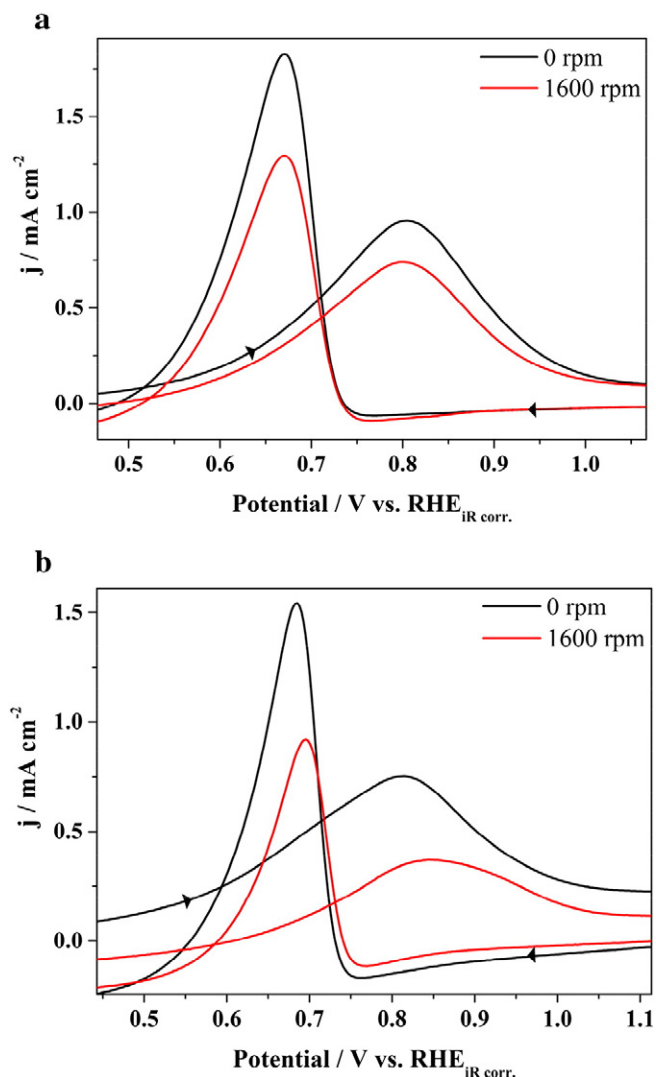


Fig. 1. a. CV of Pd/NCNT in 1 M NaOH + 1 M EtOH,  $10 \text{ mV s}^{-1}$  scan rate at 0 and 1600 rpm. b. CV of Pd/OCNT in 1 M NaOH + 1 M EtOH,  $10 \text{ mV s}^{-1}$  scan rate at 0 and 1600 rpm.

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