

Carbon Nanowalls for oxygen reduction reaction in Bio Fuel Cells

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Abstract. We report on the usage of Carbon Nanowalls (CNW) synthesized by a PECVD process as electrode material for oxygen reduction reaction (ORR). In order to substitute the platinum based catalysts in fuel cells, graphene is a promising candidate. Carbon Nanowalls are a graphene modification with good accessibility and a controllable morphology. By controlling height and pore size, they can be optimized for different applications. A I_D/I_G ratio around 2.5 and the SEM images indicate vertical nanocrystalline graphene sheets. Tests with ferrocene as electroactive compound verify CNW suitability as electrode material. Cyclic voltammetry measurements in oxygen saturated PBS prove the catalytic activity of CNW towards ORR. The results support the feasibility of CNW as cathode in Bio Fuel Cells.

1. Introduction

Most bio fuel cells use platinum based materials as cathode material to reduce oxygen, although depending on the field of application different problems exist. Outside of the human body a bio fuel cell is limited by its production cost which, to a significant degree, results from using platinum [1]. Replacing platinum at the cathode would therefore offer a big gain of economic competitiveness. Inside the human body bio fuel cells do not reach the lifespan necessary to be a feasible replacement for batteries or other implant energy delivering systems. One cause is the little durability due to insufficient long term stability of platinum [2].

For these reasons the search for an adequate alternative is extensive. A popular alternative are graphene based catalysts. They are catalytic active towards oxygen reduction reaction (ORR), highly selective, conductive and durable [3]. CNW are vertical grown graphene sheets with a high surface area and a good accessibility of the surface and the edges, which can be directly grown on a conductive surface [4]. Considering that the ORR is mostly limited by the diffusion of oxygen, CNW with their inherent good accessibility and ordered morphology can have an advantage over other ORR catalysts.

In this work we present the results obtained by examination of CNW for ORR at neutral conditions. The ORR kinetics are more sluggish at neutral than in alkaline conditions, but bio fuel cells only work in environments with a neutral pH. For the examination, the nanostructure, morphology and electrochemical activity of CNW were measured and discussed.



2. Methodology

The examined CNW were synthesized on top of a titanium substrate by plasma-enhanced chemical vapor deposition (PECVD) process [5]. Titanium was chosen as substrate because of its good electrochemical stability. More details about the synthesis will be presented in further publication.

Raman spectroscopy, Scanning electron microscope (SEM) and cyclic voltammetry (CV) are used to evaluate the nanostructure, morphology and electro chemical activity of the CNW.

For the Raman spectroscopy an Olympus BX40 with a laser light of 633 nm was used. The SEM Images were taken using a Quanta FEG 250.

For electro chemical measurements, a three electrode cell with Ag/AgCl as the reference electrode and platinum sheet as the counter electrode was used. In order to examine whether the CNW are conductive and therefor applicable as electrodes, the first test measurements were performed in a 5mM ferrocene acetonitrile solution with tetrabutyl ammonium hexafluorophosphate as electrolyte. Two cyclic voltammetry scans were carried out at a scan rate of 10 mV/s in the potential range of 0.1 V to 0.7 V. The second scan was used for evaluation.

The ability of CNW to enhance ORR was investigated in phosphate buffered aqueous solution (PBS) with a pH of 7.4. To confirm ORR, measurements were carried out in nitrogen and oxygen saturated electrolyte. In addition, the ORR was tested for Glassy Carbon for comparison. Two cyclic voltammetry scans were carried out at a scan rate of 5 mV/s in the potential range of -0.6 V to 0.4 V.

3. Results and discussion

Figure 1 shows a Raman spectrum of the synthesized CNW. The D peak at 1331 cm^{-1} and the D' peak at 1616 cm^{-1} are an indicator for disorder in molecular structure, while the G peak is attributed to graphitic structure with sp^2 hybridized carbon. The I_D/I_G ratio of 2.48 evidences a high amount of defects originated from the high edge density typical for CNW. The position of the G peak at 1595 cm^{-1} indicates a nanocrystalline graphite structure with little or no amorphous carbon [6][7].

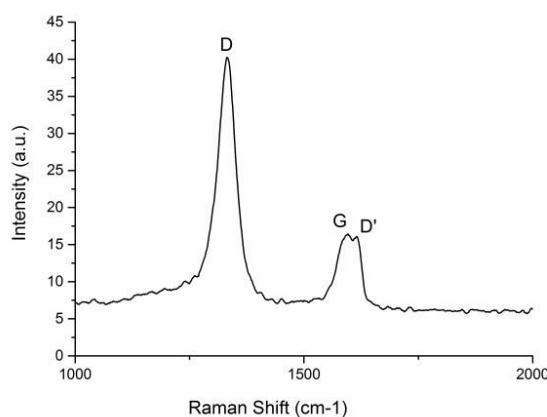


Figure 1. Raman spectrum of the CNW sample showing the peaks of the D, D' and G band.

A macroporous structure is confirmed by SEM images (Figure 2). In Figure 2a, the surface and cross section of the CNW are depicted. The CNW are homogeneously distributed over the substrate and are approximately $1.2\text{ }\mu\text{m}$ in height. Figure 2b exhibits the walls with length of roughly 150 nm. The walls grew disorderly upwards creating a macroporous structure, which allow for the fast fuel transport through the CNW network.

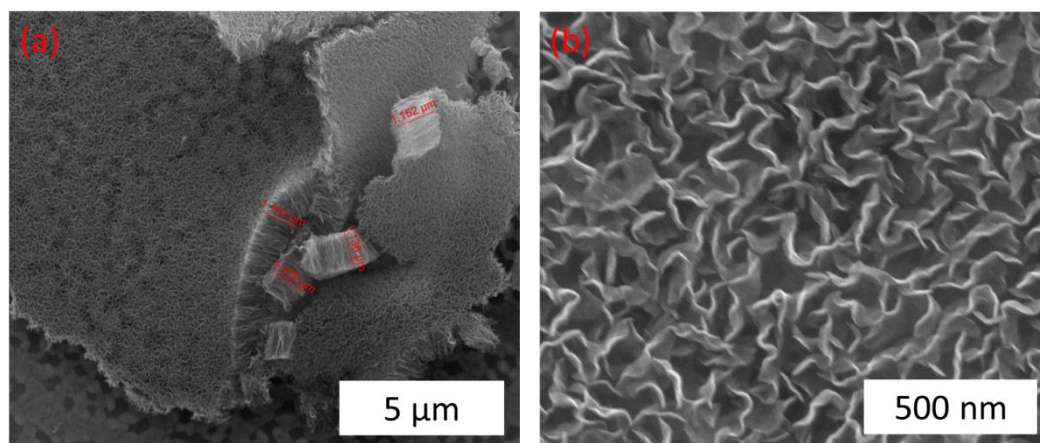


Figure 2. SEM pictures of the characterized CNW sample: (a) the surface and the cross section and (b) the surface morphology.

Figure 3 shows a cyclic voltammogram of 1 electron ferrocene oxidation performed using a CNW electrode. The high current density of the oxidation confirms the electrical conductivity and electroactivity of CNW. The potential difference ΔE_p between the anodic peak potential E_{pa} and the cathodic peak potential E_{pc} is less than 0.1 V. The theoretical value for ΔE_p for a reversible 1 electron process is 0.057 V. Large values of ΔE_p indicate slow electron transfer kinetics. Considering the large electrode area of 0.28 cm² and the high electrode surface which result in a high current density and thus high electrode resistance, the observed potential difference reveals a quite fast charge transfer on CNW electrode and proves CNW suitability for electrode application[8].

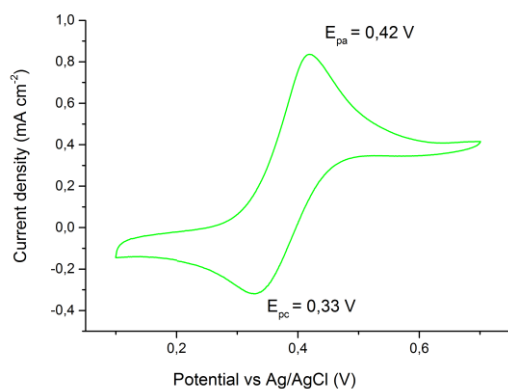


Figure 3. Cyclic voltammogram of ferrocene oxidation performed at a scan rate of 10 mV/s.

The CNW capability for oxygen reduction is shown in Figure 4a by means of CV experiments performed in nitrogen saturated (black line) and in oxygen saturated PBS solution at a pH of 7.4 (red line). At around -0.15V the oxygen reduction starts visibly increasing the cathodic current. Figure 4b compares the ORR on CNW and Glassy Carbon electrode in solution saturated only by oxygen. The onset potential for ORR is anodically shifted by 0.2 V for CNW compared to Glassy Carbon indicating catalytic activity towards oxygen reduction.

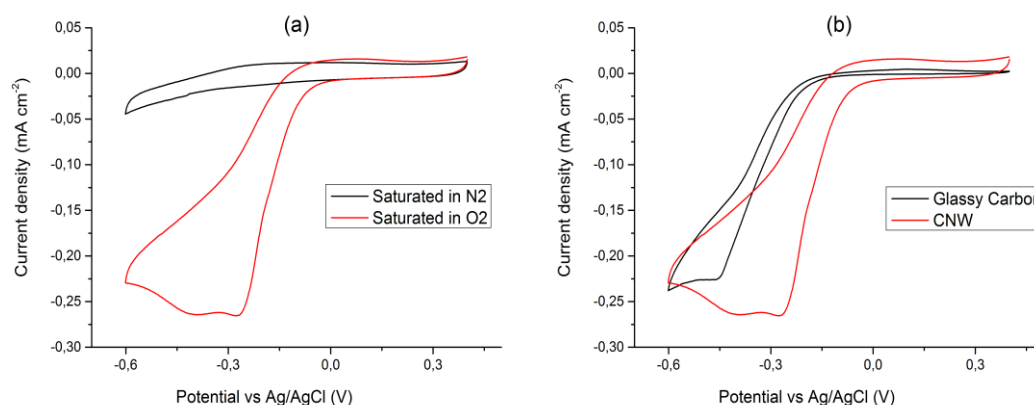


Figure 4. Cyclic voltammogram of (a) CNW electrode in a nitrogen and oxygen saturated PBS solution at a pH of 7.4 and (b) a Glassy Carbon electrode compared with a CNW electrode in an oxygen saturated PBS solution.

4. Conclusion

The results of this paper show for the first time the feasibility of CNW for ORR at neutral conditions and its potential for fuel cell application. The structure of investigated CNW was examined by RAMAN and SEM. RAMAN results indicated a nanocrystalline graphitic structure with little or no amorphous carbon. The SEM results confirm the formation of porous network from vertical aligned graphene sheets. The electrochemical applicability of CNW as electrode was tested by means of reversible oxidation of ferrocene. The oxidation of ferrocene was kinetically reversible confirming CNW as suitable electrode material. The catalytic activity of CNW for ORR was proved by comparison with Glassy carbon electrode. The comparison shows a shifted onset of ORR for CNW, revealing catalytic properties.

The results evidence, that CNW is a promising cathode material for bio fuel cells. In the future, the experiments for improving the electrochemical properties of CNWs by means of adjustment the material morphology and structure will be performed even further. In addition, the resulting CNW will be compared to graphene and platinum cathode.

5. Acknowledgment

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