



Short communication

Development of a self-supported single-wall carbon nanotube-based gas diffusion electrode with spatially well-defined reaction and diffusion layers

J.-F. Drillet^{a,*}, H. Bueb^a, U. Dettlaff-Weglikowska^b, R. Dittmeyer^a, S. Roth^b

^a DECHEMA e.V., Society for Chemical Engineering and Biotechnology, Karl Winnacker Institute, Theodor-Heuss-Allee 25, 60486 Frankfurt am Main, Germany

^b Max Planck Institute for Solid State Research, Heisenbergstraße 1, 70569 Stuttgart, Germany

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ABSTRACT

This work reports on the development of a solvent-free method for the fabrication of a self-supported single-wall carbon nanotubes electrode, which is based on successive sedimentation of both SWCNT/surfactant and PtRu–SWCNT/surfactant suspensions followed by a thermal treatment at 130 °C. The as-prepared self-supported electrode showed sufficient mechanical strength for half-cell investigation and membrane-electrodes assembly fabrication. By using a Pt catalyst loading of 1 mg cm⁻², the overall thickness of the gas diffusion electrode reached 95 μm. Its electrochemical activity towards methanol oxidation was investigated by means of cyclic voltammetry and current–voltage polarisation measurements under half-cell and direct methanol fuel cell conditions.

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1. Introduction

The fabrication of gas diffusion electrodes relies usually on complicated spraying or screen-printing techniques for coating the diffusion and reaction layer on the carbon cloth or carbon paper backing. The efficiency of these composite electrodes depends not only on the catalyst activity but also on their structure and morphology. They should have high electronic conductivity, specific area and corrosion resistance, and additionally facilitate optimal mass transport of reactants and products. Carbon nanotubes (CNTs) possess most of the required properties and appear to be an interesting substitution material for carbon fibre and carbon powder in gas diffusion electrodes, which are more vulnerable to corrosion and less conductive [1]. With the help of a surfactant, single-wall carbon nanotubes (SWCNTs) can be easily shaped into a so-called buckypaper [2]. Since high metal ratio in the carbon nanotube suspension weakens the carbon network, already published works report only on metal-free buckypaper fabrication. The first “Free-standing” SWCNT-based electrodes were synthesised by Ng et al. [3] and tested as an anode material for the Li-Ion battery. Kaempgen et al. [4] have prepared a self-supported electrode with hydrophobic and hydrophilic SWCNT layers for phosphoric acid fuel cell applications. After washing the buckypaper, a Pt precursor solution was poured over the hydrophilic layer and annealed

at 100 °C under hydrogen flow to obtain metallic platinum. The present work describes a simple method for fabrication of GDEs based on successive sedimentation of the SWCNT/surfactant and PtRu–SWCNT/surfactant suspension that leads to the formation of two spatially well-defined diffusion and reaction regions.

2. Experimental

The single-wall carbon nanotube material was produced by arc-discharge evaporation of a 6-mm graphite rod filled with a Ni and Y (4:1 weight %) powder (Yangtze Nanotechnology, Shanghai, China). The reaction took place under helium atmosphere at 500 mbar, 100 A and 50 V. The as-prepared raw material contained a significant amount of impurities, such as amorphous carbon and residual Ni and Y catalyst particles. The purification and chemical functionalisation of the raw material as well as its characterisation by near-infrared spectroscopy (NIR), inductive coupled plasma (ICP) and thermogravimetric analysis (TGA) were performed at the Max Planck Institute for Solid State Research (Group of Synthetic Nanostructures, Stuttgart, Germany). The results of these investigations are reported elsewhere [5]. The fabrication of the self-supported electrode was carried out as follows: For the diffusion layer, 40 mg of pristine SWCNT were dispersed in 40 ml of a 1 wt% sodium n-dodecyl sulphate solution (99% purity, Alfa Aesar GmbH, Karlsruhe, Germany) by high-energy ultrasonic agitation (type Sonifier Branson, G. Heinemann GmbH, Schwäbisch Gmünd, Germany) for 10 min. The amount of a 30 wt% PTFE/water suspension was adjusted to obtain a PTFE:SWCNT weight ratio of

* Corresponding author. Tel.: +49 697564 476; fax: +49 697564 388.

E-mail address: drillet@dechema.de (J.-F. Drillet).

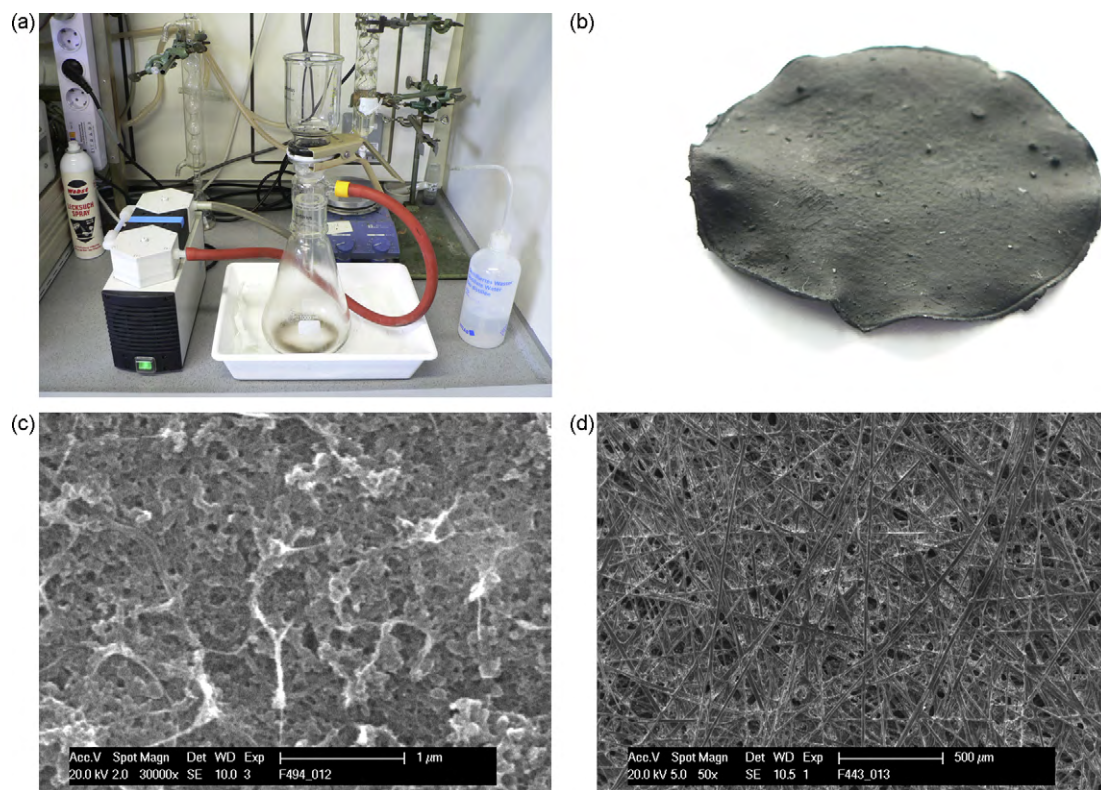


Fig. 1. (a) Filtration apparatus with vacuum pump; (b) and (c) self-supported SWCNT electrode; and (d) Toray Carbon Paper (TGP-H-60).

20:100. For the reaction layer, SWCNTs were previously treated and functionalised in hot air at 300 °C and decorated with PtRu according to the chemical impregnation method described in Ref. [6]. The catalyst:substrate weight ratio was fixed to 60:100 whereas the Pt:Ru atomic ratio was 1:1 and the Pt loading 1 mg cm^{-2} . Then 62 mg of SWCNT-supported PtRu catalyst were dispersed in 40 ml of a 1 wt% sodium n-dodecyl sulphate (99%, Alfa Aesar) solution by high-energy ultrasonic agitation (type Sonifier, Branson) for 10 min. The amount of NafionTM and PTFE was adjusted to obtain a weight ratio of 10 and 20% of the PtRu–SWCNT mass, respectively. The fabrication process of the self-supported SWCNT electrode was carried out by successive filtering of the suspensions, peeling off of the filter cake from a 0.4-μm pore size membrane of mixed cellulose ester (Millipore GmbH, Schwalbach, Germany) and sintering at 130 °C for 20 min in order to enhance the adhesion of the polymer compounds. SEM pictures were performed with a XL-40 Philips microscope. The element concentration within the self-supported electrode was determined with an electron probe micro-analyser (EPMA, Type JEOL JXA-8100, Eching, Germany). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed by a potentiostat/galvanostat (type 273, EG&G, GAMEC GmbH, Illingen, Germany) coupled with a frequency generator (type SI 1255, Schlumberger GmbH). Membrane-electrodes-assemblies (MEAs) were fabricated by pressing together the as-prepared anode with a NafionTM 117 membrane (Ion-Power Inc., New Castle DE, USA) and a commercial cathode (QuinTech GmbH, Göppingen, Germany) at 6 bar, 130 °C for 4 min, and tested in a 5 cm² commercial DMFC (QuinTech GmbH, Germany). Both electrodes were previously sprayed with 1 mg cm^{-2} NafionTM in order to enhance their adherence with the polymer membrane and to enlarge the ion-conducting zone within the reaction layers. The flow feed and backpressure of methanol and oxygen/nitrogen were set to $10 \text{ ml min}^{-1}/1.3 \text{ bar}_{\text{abs}}$ and $300\text{--}500 \text{ ml min}^{-1}/1.1 \text{ bar}_{\text{abs}}$, respectively.

3. Results

Preliminary tests were carried out in order to select the most appropriate material for the diffusion layer of the self-supported electrode principally with respect to its mechanical strength. The best structures were obtained with pristine SWCNT in comparison with those based on SWCNT previously treated either in nitric acid or in hot air at 300 °C for purification purposes. Since the mechanical stability of nanotube networks strongly depends on the aspect ratio and the flexibility of the entangled ropes, some weakness can be expected after chemical treatment when shorted, rigid nanotube bundles have been combined into a paper structure. The choice of air-treated SWCNTs as PtRu catalyst supports for the anodic reaction layer was motivated by the excellent results obtained with this system during former experiments under DMFC conditions for which a Toray carbon Paper (type TGP-H-60) was utilised as a backing layer [5].

The filtration set-up and a self-supported PtRu–SWCNT/SWCNT (42 mm in diameter) are shown in Fig. 1a and b, respectively. SEM pictures reveal a very compact structure with pore sizes in the range of 0.1–1 μm for the self-supported SWCNT electrode surface (Fig. 1c) compared to that of a commercial Toray Carbon Paper (Fig. 1d).

A microscope image of the cross-section of a self-supported SWCNT electrode and its corresponding elemental analysis are shown in Fig. 2. The overall thickness of the electrode amounts about 95 μm. On the left picture, the excellent bonding of both layers is obvious. Although one can visually distinguish the reaction layer from the diffusion layer because of its somewhat higher light reflection due to the presence of metal particles confirmed by the element analysis shown in Fig. 2b. In the reaction layer, platinum, ruthenium and oxygen prevail, and are well-dispersed, with the exception of some agglomerated particles. Regions with high ruthenium level also exhibit high oxygen concentration as well, which is an indication of ruthenium oxide formation. No metallic traces are

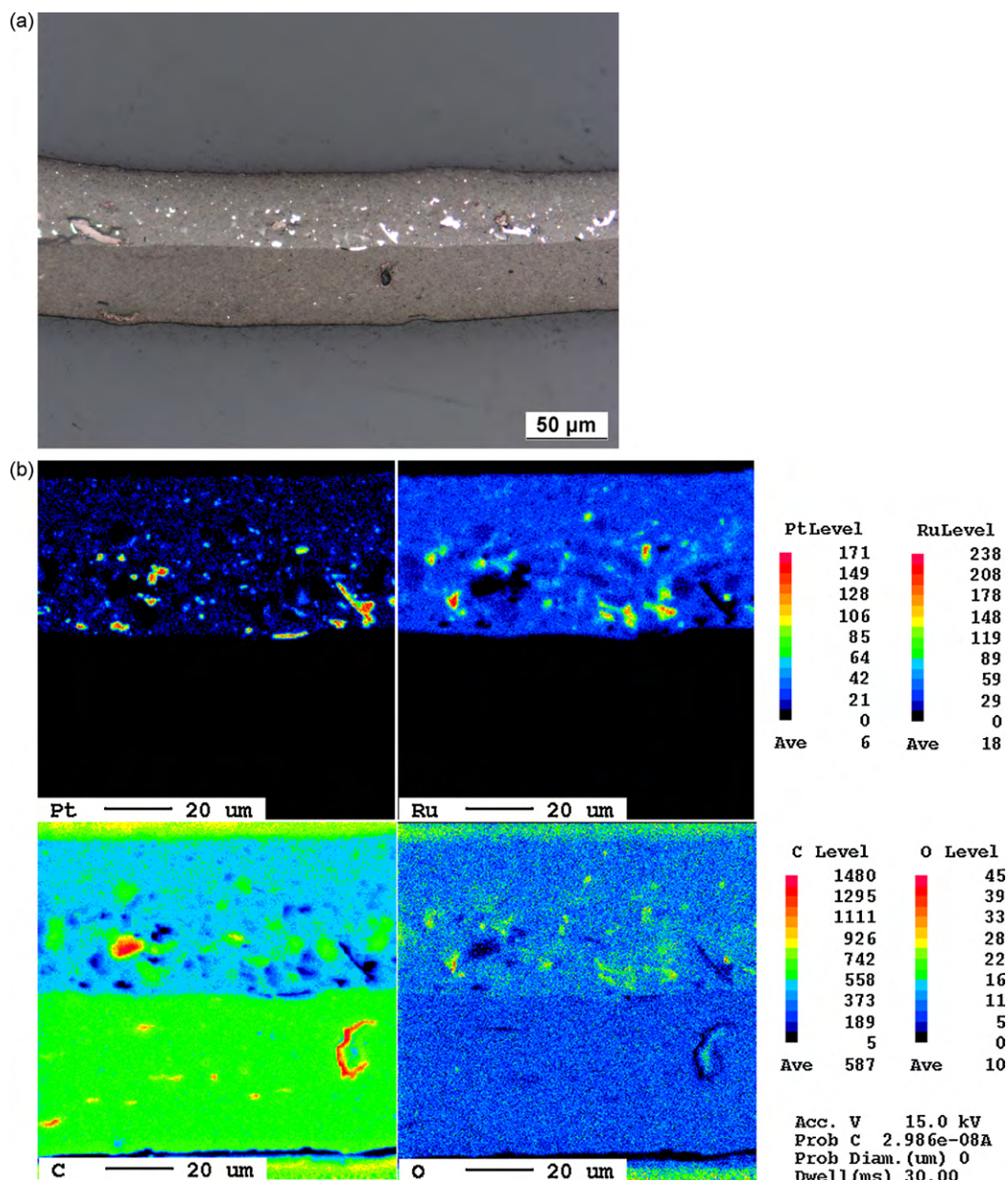


Fig. 2. (a) Cross-section and (b) element analysis of the self-supported PtRu-SWCNT/SWCNT electrode.

visible in the diffusion layer, which is primarily composed of pure carbon.

The electrochemical activity of the self-supported electrode was investigated in a half-cell by means of cyclic voltammetry in pure 1.0 M sulphuric acid (Fig. 3a) and in 1.0 M sulphuric acid containing 2.0 M methanol (Fig. 3b) at room temperature. In order to minimize Ru dissolution, the potential window of the measurement in pure sulphuric acid was first limited to 0–500 mV vs. RHE. In this potential window, capacitive behaviour due to high ruthenium oxide coverage dominates. For the examination of methanol oxidation, the potential window was extended to 1.2 V. A potential shift of the onset potential of the anodic methanol oxidation of about 100 mV to more positive values was observed during the first 50 cycles. This is an indication of rapid Ru dissolution. The next 50 cycles were quite stable and are shown in Fig. 3b. The self-supported PtRu-SWCNT/SWCNT exhibits a high specific activity for methanol oxidation during anodic scanning at about 900 mV and room temperature, which is comparable to the activity of common Pt-Vulcan-based systems.

In the following experiment, a 1 mg cm^{-2} PtRu-SWCNT/SWCNT in-house-made anode was pressed together with a commercial NafionTM 117 membrane and a 1 mg cm^{-2} Pt-Vulcan/C cathode to form a MEA. A microscope picture of the cross-section of such a MEA is presented in Fig. 4. It shows an exceptionally high bonding quality of the self-supported SWCNT electrode and more precisely of its reaction layer with the NafionTM membrane compared to that of the Pt-Vulcan/membrane boundary. Moreover, in contrast to the commercial electrode where some hollow regions appear between the carbon fibres (white areas) in the reaction layer, the self-supported electrode is characterised by a high homogeneity. Average thickness values of 95, 170 and $250 \mu\text{m}$ were measured for the self-supported anode, electrolyte and cathode, respectively.

The MEA was tested with respect to methanol activity, ohmic resistance and methanol permeation under fuel cell conditions at 80°C . The results of the polarisation measurements under pure oxygen and synthetic air atmospheres are shown in Fig. 5. A maximal power density of 22 mW cm^{-2} was reached with pure oxygen at 80 mA cm^{-2} current density, which corresponds to approxi-

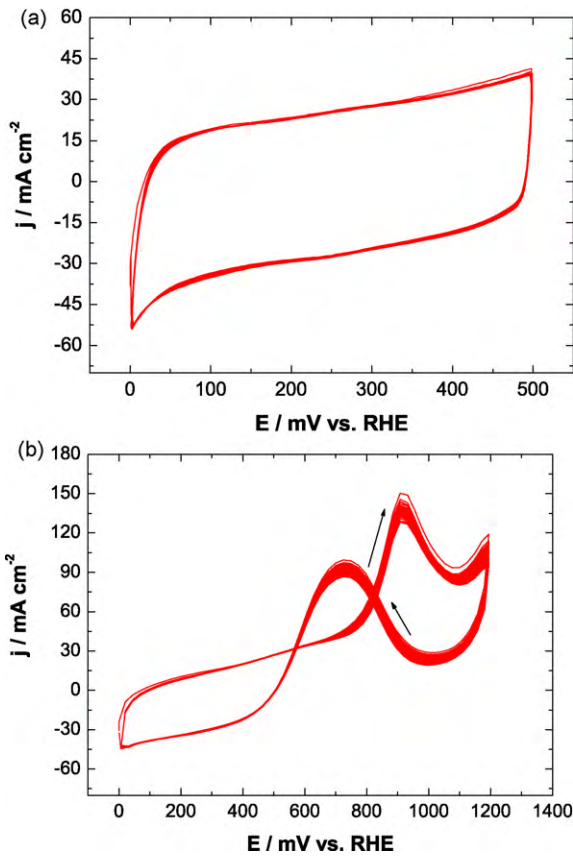


Fig. 3. Fifty cyclic voltammograms of a 1 mg cm^{-2} PtRu-SWCNT/SWCNT gas diffusion electrode in (a) $1 \text{ M H}_2\text{SO}_4$ and (b) $1 \text{ M H}_2\text{SO}_4 + 2 \text{ M CH}_3\text{OH}$ at 40 mV s^{-1} and at room temperature.

mately one seventh of the values collected at a MEA with a PtRu-SWCNT/TGP-H-60 anode during previous experiments [5]. Attempts to increase the power density by setting higher pressure for methanol and oxygen were not successful. This is an indication of mass transport limitation of methanol or/and carbon dioxide within the diffusion and reaction layers or/and insufficient catalyst utilisation. Another drawback of the self-supported electrode is its relatively low through-plane mechanical resistance at high cathode pressure in comparison with that of, e.g. a Toray carbon Paper supported electrode. As a consequence, the MEA may locally penetrate into the methanol flow fields and hinder proper fuel distribution. This problem can be solved by narrowing the channel width.

The performance in the fuel cell is obviously affected by the high ohmic resistance close to 0.6Ω measured during the impedance measurement (EIS) at high frequencies (see Fig. 6). This is mostly due to the use of pristine SWCNTs in the diffusion layer that contain about 65% impurities such as amorphous carbon and encapsulated residual catalysts (Ni, Y) from the fabrication process [5].

In order to study the influence of the SWCNT-based anode on methanol permeation within the composite MEA, the DMFC was connected in electrolysis mode. For this purpose, the cathode and the anode chambers were fed with a $1 \text{ M CH}_3\text{OH}$ solution and nitrogen gas, respectively. In the case of the conventional MEA with VulcanXC72-based electrodes, the methanol oxidation rate at the anode is limited by the methanol diffusion through the NafionTM membrane [7]. Since hydrogen evolution takes place in the cathode chamber fed with $1 \text{ M CH}_3\text{OH}$, it can be considered as a reference electrode. This method was primarily applied here to obtain some qualitative information about the influence of the SWCNTs on methanol permeation within the MEA. Since all tested MEAs are made of the same commercial NafionTM117 membrane and

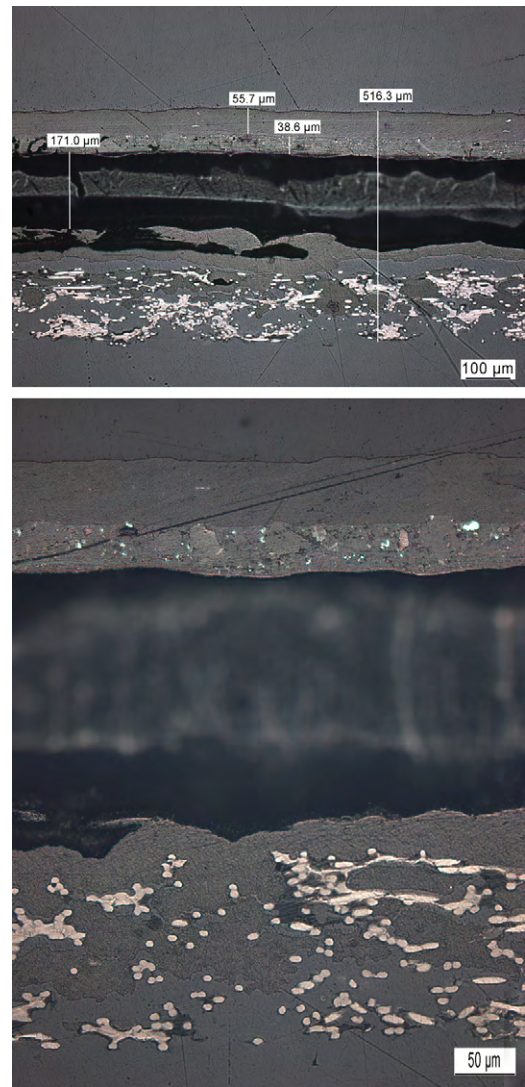


Fig. 4. Optical micrograph of a MEA at different magnifications with a self-supported PtRu-SWCNT/SWCNT anode (top), NafionTM117 membrane (middle) and Pt-Vulcan/C cathode (bottom).

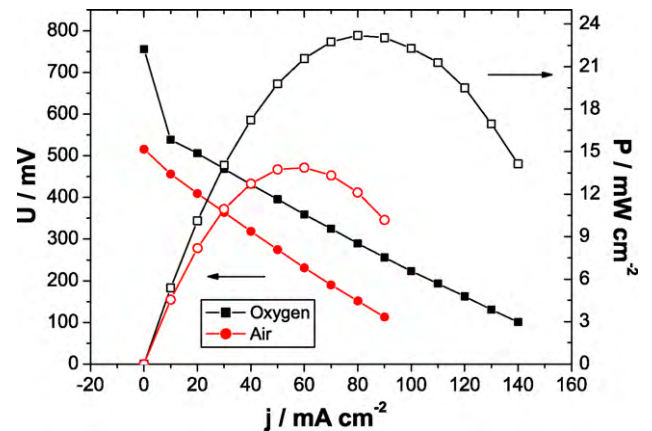


Fig. 5. Polarisation curve of a MEA with a self-supported anode at $80 \text{ }^\circ\text{C}$ and 1.3 and 1.1 bar_{abs} methanol and oxygen/air pressure, respectively.

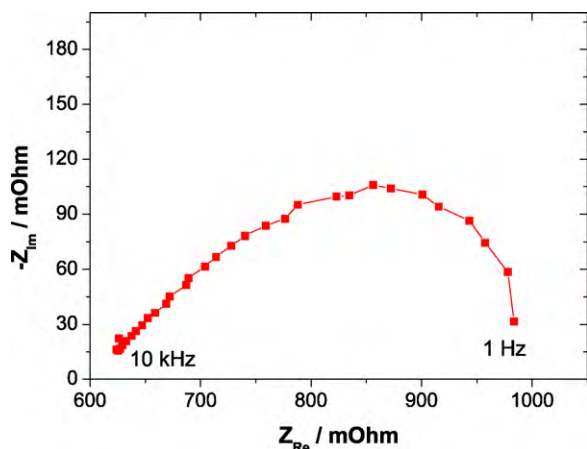


Fig. 6. Nyquist plot of a MEA with a self-supported anode at 500 mA, 80 °C and 1.3 and 1.1 bar_{abs} methanol and oxygen pressure, respectively.

the same commercial Pt–Vulcan electrode (anode in electrolysis mode), any change in the kinetic- or diffusion-controlled region observed during methanol oxidation at the Vulcan-based anode (electrolysis mode) can be attributed to the SWCNT-based counter electrode. In Fig. 7, the limiting current for methanol oxidation at the conventional Vulcan-based MEA amounts to 155 mA cm⁻²,

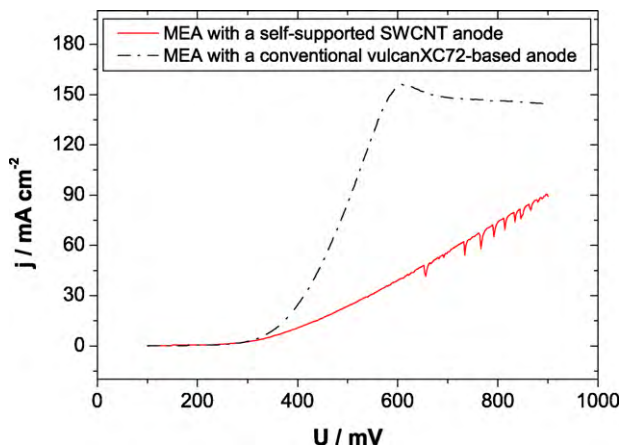


Fig. 7. Methanol permeation measurements for different MEAs connected in electrolysis mode at 1 mV s⁻¹, 80 °C, 1.3 and 1.1 bar_{abs} methanol and nitrogen pressure, respectively.

which is in good agreement with the value reported in Ref. [7]. In this case, the limiting current is controlled by the methanol flux through the NafionTM117 membrane.

In the case of the MEA with the self-supported SWCNT-based cathode (electrolysis mode), the kinetically controlled region of the methanol oxidation is strongly affected by the ohmic resistance of the MEA. Even at high potential values no limiting current plateau was detected.

4. Conclusion

For the first time, a self-supported carbon nanotubes electrode was fabricated by successive sedimentation of SWCNT/surfactant and highly metal-loaded SWCNT/surfactant suspensions followed by a sintering process at 130 °C. Hydrophobic and ionic conductivity properties of both layers were achieved by adding appropriate amounts of PTFE and NafionTM to the corresponding suspension. The as-prepared electrodes showed sufficient mechanical strength for investigations in the half-cell and DMFC. Optical micrographs of the MEA revealed excellent bonding of the self-supported carbon nanotube electrode with the NafionTM117 polymer membrane. A maximal power density of 22 mW cm⁻² was measured at a MEA with a 1 mg cm⁻² PtRu–SWCNT/SWCNT self-supported anode under oxygen atmosphere. Further work will focus on the enhancement of the catalyst accessibility and decrease of the ohmic resistance of the pristine SWCNT-based diffusion layer.

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