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Activity and long-term stability of PEDOT as Pt catalyst support for the DMFC anode

J.-F. Drillet · R. Dittmeyer · K. Jüttner

Abstract The feasibility of using poly(3,4-ethylenedioxythiophene) (PEDOT) as Pt catalyst support for direct methanol fuel cell (DMFC) anodes was investigated. Measurements with freshly prepared Pt-PEDOT/C electrodes showed poor activity for methanol oxidation in a half-cell and a DMFC. A substantial enhancement in that activity was evident after either electrochemical over-oxidation of PEDOT or long-time storage of the Pt-PEDOT/C gas diffusion electrode (GDE) in air. Both procedures led to a reorganization and increase in porosity of the reaction layer, which obviously contributed to better methanol accessibility to Pt catalyst active centres. The effects of electrochemical activation and long-time storage in air on the morphology and elementary composition of the Pt-PEDOT layer were investigated by means of Hg porosimetry and SEM/EDAX. It was found that the increase in porosity was due to degradation of PEDOT characterized by a significant depletion of sulphur and oxygen in the conducting polymer matrix.

Keywords Catalyst support · Conducting polymer · DMFC · Over-oxidation · PEDOT

1 Introduction

Most of the common conjugated organic polymers behave either as insulators or as semi-conductors. Since the discovery of "metallic" polyacetylene formed after exposure to bromine or iodine vapour [1], several other methods,

such as photo-excitation, chemical and electrochemical redox doping and charge injection have been developed in order to induce electronic conductivity, which can achieve values close to those of magnesium or copper [2]. Only doping methods, or more precisely intercalation, yield a permanent transition to the conductive state. The π-electron delocalization in the polymer backbone is responsible for the change of their electronic and/or optical properties. An exhaustive review of the synthesis and characterization of conjugated polymers is given in [3].

Among the numerous polyaniline (PAni), polypyrrole (PPy) or polythiophene based conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives appear to be one of the most promising candidates for commercial applications [4]. The photodiode (LED), nano-switcher, polymer-dispersed-liquid-crystal-display (PDLC), field-effect transistor (FET), biosensor, glass coating and antistatic treatment are the more relevant products that have issued from the conducting polymer family. The monomer 3,4-ethylenedioxythiophene (EDOT) was developed by Bayer Technology Services and its derivate product family is commercialized under the trade name Baytron®. Films with high-electronic conductivity between 200 and 1,000 S cm^{-1} can be obtained under appropriate conditions by chemical oxidation of EDOT.

The solubility and long-term stability of PEDOT were enhanced by poly(styrenesulfonate) (PSS) blending. In spite of its lower electronic conductivity compared to that of PEDOT, PEDOT-PSS is widely used as a cathode material in tantalum, niobium or aluminium capacitors instead of manganese dioxide. The advantages of PEDOT-PSS compared to manganese dioxide [5] include: 10^3 times higher electronic conductivity, lack of ignition risk and easier electrode manufacturing. The specific capacitance of supercapacitors was enhanced by using single-walled carbon

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nano-tube (SWNT)/PPy [6] and PEDOT/PPy [7] composite electrode materials.

The mixed ionic and electronic conductivity of some CP, such as PAni, PPy or PEDOT also makes them interesting for hydrogen [8] and methanol [9, 10] fuel cell applications, especially for the development of more efficient catalyst supports. In this case, theoretically only a two-phase boundary is necessary for electron and ion transfer during methanol oxidation in the direct methanol fuel cell (DMFC) compared to the three-phase boundary when carbon is used. The substitution of carbon by PEDOT or PEDOT-PSS should lead to better catalyst utilization. However, Shan and Pickup [11] found a 30–70% lower Pt utilization with chemical synthesized PEDOT-PSS as catalyst support. Shen et al. [12] reported no methanol activity for electrochemically deposited Pt on a PEDOT-PSS film and a loss in DMFC performance when PEDOT is added in the anode and cathode catalyst layers.

The performance of the DMFC is limited mainly by the poor activity of the anode catalyst for methanol oxidation, which is due to adsorbed reaction intermediates, such as carbon monoxide, and by the methanol crossover, which contributes to the formation of a mixed potential at the cathode. The negative influence of the methanol crossover can be attenuated by incorporation of methanol-tolerant cathode catalysts, such as Pt–Ni alloy [13, 14] and by membranes less permeable to methanol. The modification of Nafion® 117 membranes by chemical polymerization of PEDOT was described in a recent paper [15]. The methanol permeation rate and, unfortunately, the fuel cell performance decreased with increasing thickness of the PEDOT layer. The decrease in the fuel cell performance was explained by the preponderant influence of the loss in the proton conductivity of the composite membrane, compared to that of its decreased methanol permeation rate.

The efficiency of the reaction layer relies, among other things, on good accessibility of the reactants to the nano-particle catalyst and simultaneous transport away of the reaction products, which depends on appropriate porosity and hydrophilic/hydrophobic balance. Rajesh et al. [16] have reported an activity for methanol oxidation at Pt supported on PAni-based nano-tubes that was twice that of a conventional Pt-VulcanXC72 system.

Our preliminary experiments dealt with the characterization of PEDOT and PEDOT-PSS as gas diffusion electrode (GDE) and Pt catalyst support materials for the DMFC anode [17]. PSS-blended PEDOT systems prepared with $FeCl_3$ or $Na_2S_2O_8$ as oxidizing agents showed a higher onset potential of the anodic charging reaction and higher impedance compared to those of the PSS-free PEDOT/$Na_2S_2O_8$ system. Freshly prepared Pt-PEDOT/C anodes exhibited poor activity for methanol oxidation in half-cell measurements at room temperature. After partial over-

oxidation of PEDOT, a significant enhancement of the Pt activity with respect to methanol oxidation was observed at 60:100 weight ratio Pt : PEDOT. The higher activity was assumed to be the consequence of an increase in porosity of the reaction layer, discernible on the SEM photomicrographs. EDAX investigations revealed a large depletion of S and O in the polymer matrix. FTIR spectra confirmed that the electrochemical activation process leads to conducting polymer degradation and particularly to partial decomposition of the thiophene ring [17]. In order to preserve ionic and electronic mixed conductivity of the catalyst support, over-oxidation of the conducting polymer should be avoided.

The present work focuses on the further development of a PEDOT-based anode and its performance evaluation in a DMFC with a commercial Nafion 117 membrane and Pt-VulcanXC72/C cathode. In situ measurements of methanol permeation in the fuel cell, SEM/EDX and Hg porosimetry should contribute to a better understanding of the PEDOT behaviour as catalyst support in a DMFC anode.

2 Experimental

The development of the composite anode includes the preparation of the conducting polymer powder and catalyst deposition, the ink formulation, the electrode coating with the brush painting or spray method, its characterization in a cell designed for GDE, hot pressing of the membrane-electrodes assembly (MEA) and finally, its test in the DMFC. A 0.2 M EDOT solution (H.C. Starck GmbH, Goslar, Germany) was mixed with 0.2 M $Na_2S_2O_8$ and stirred for 2 days at room temperature. After polymerization, the PEDOT suspension was filtered and washed several times with de-ionized water in order to release the residual monomer and oxidizing agent. Finally, the filtrate was dried at 60 °C for 5 h.

The catalyst : substrate weight ratio was fixed at 60:100. The catalyst support was either PEDOT or VulcanXC72 (Cabot GmbH, Hanau, Germany). The chemical Pt catalyst deposition on 100 mg of substrate was carried out with 180 mg (13% surplus) of a $H_2[PtCl_6]\cdot6H_2O$ precursor (Aldrich GmbH, Steinheim, Germany) dissolved in 25 cm³ of 37% formaldehyde solution stabilized in 10% methanol (Merck KgaA, Darmstadt, Germany) and stirred at 80 °C for 1 h. After cooling, the suspension was washed with de-ionized water, filtered through a 0.025 μm filter membrane of mixed cellulose esters (Millipore, Inc., Bedford, MA, USA) and dried at 60 °C for 5 h. A Pt yield close to 100% was obtained for both catalyst-supported powders. The catalyst-substrate powder was mixed with a volumetric ratio of 1:2 or 1:3 water : 2-propanol solution and

ultrasonicated for 15 min. The amount of 10 wt.% Nafion and 20 wt.% PTFE (Ion Power Inc., New Castle, DE, USA) was successively added to the suspension and ultrasonicated for 15 min. The GDEs were prepared by coating the backing layer (Toray carbon paper TGP-H-60) either by brush painting or spray method, depending on the electrode area. The Pt catalyst loading was fixed at 1 mg cm^{-2} both for the anode and the cathode. The coating process included 15–20 coating steps, sintering processes at 80 °C for 4 min between each layer, and finally, a sintering step at 100 °C for 30 min.

MEAs were fabricated by hot pressing together the anode made in-house, the Nafion 117 membrane (Ion-Power Inc.) and the commercial cathode (QuinTech GmbH, Indiana, PA, USA) at 6 bar, 130 °C for 4 min and tested in a 5 cm^2 commercial DMFC purchased from QuinTech GmbH. The Nafion 117 membrane was treated successively by boiling in 3% H_2O_2, 1 M H_2SO_4 and distilled water for 1 h each. The methanol and oxygen/nitrogen flow feed was 10 and 300–400 cm^3 min^{-1}, respectively.

The electrochemical characterization of the Pt-PEDOT based GDE was carried out in a three-electrode Plexiglas cell in 1 M H_2SO_4 or 1 M H_2SO_4 + 2 M CH_3OH solution. The effective geometrical area of the sample was 0.5 cm^2. A Princeton Applied Research 273 potentiostat was used for cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronoamperometry (CA).

SEM/EDAX and Hg porosimetry measurements were made with a XL-40 Philips-EDAX microscope and a Porosimeter 2000 (Carlo Erba Instruments, Limito, Italy, Porotec GmbH, Hofheim, Germany), respectively.

3 Results and discussion

Figure 1 shows cyclic voltammograms of 1 mg cm^{-2} Pt-PEDOT/C in 1 M H_2SO_4 before and after activation under half-cell conditions. The activation process consisted of extending the potential window to an upper limit of 1.5 V versus a reversible hydrogen electrode (RHE). Under these conditions, irreversible over-oxidation of PEDOT occurred. The electrochemical response of the conducting polymer decreased, while the Pt characteristics became more pronounced. In the case of a freshly prepared Pt-PEDOT/C GDE, the steady-state voltammogram was obtained after 50–75 cycles and was comparable to that of polycrystalline Pt in 1 M H_2SO_4. The first 20 cycles of the electrochemical activation process are shown in Fig. 2a. The continuous diminution of the anodic current plateau, the potential shift of the PtO reduction peak to more positive potentials and the decrease of the PEDOT redox charge were associated with the over-oxidation and degradation of PEDOT [17]. The mechanisms of anodic

over-oxidation of CP are quite complex and remain controversial. However, according to Pud [18], these fall approximately into two categories: cross-linking and nucleophilic attack of the polymer chain. In Fig. 1, the presence of hydrogen adsorption and desorption regions even before activation, suggested that the hypothesis of strong Pt poisoning by sulphur from the thiophene group could be excluded.

In order to examine the long-term stability of Pt-PEDOT, the same activation procedure was applied to a 1-month-old sample, which had been stored in air and daylight at room temperature. In Fig. 2b, the anodic plateau of the first voltammogram reached a current density of about 15 mA cm^{-2}, compared to 100 mA cm^{-2} of the freshly prepared GDE in Fig. 2a. The steady state was already achieved after about 15 cycles and only a slight potential shift of the PtO reduction peak was evident. The substantial loss of the PEDOT redox activity after 1-month's storage in air, clearly reflected significant time-dependent changes in the polymer matrix.
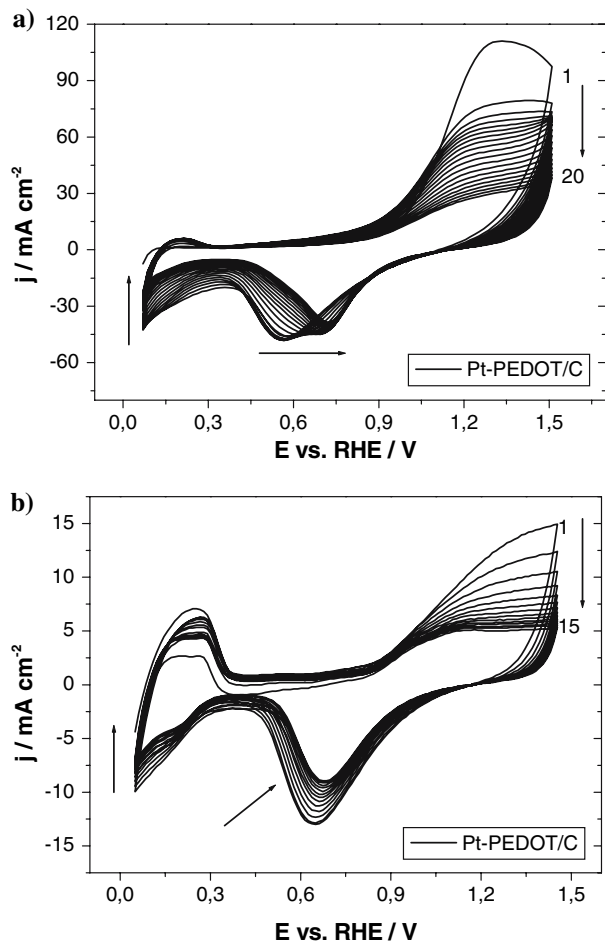
In Fig. 3, comparative linear sweep voltammograms of a freshly prepared Pt-PEDOT/C electrode illustrate the influence of the electrochemical activation process on Pt catalyst activity with respect to methanol oxidation. The current density measured at 60 °C and 800 mV increases from 300 mA cm^{-2} before, to 1,100 mA cm^{-2} after, electrochemical activation. Presumably, the reorganization of the Pt-PEDOT structure generated additional micro- and nano-channels that facilitate methanol accessibility to the catalyst centres and de facto enhance the rate of methanol oxidation.

The following investigations should elucidate whether the thickness of the PEDOT layer plays a major role in methanol accessibility and distribution within the reaction layer. For this purpose, the Pt catalyst loading was
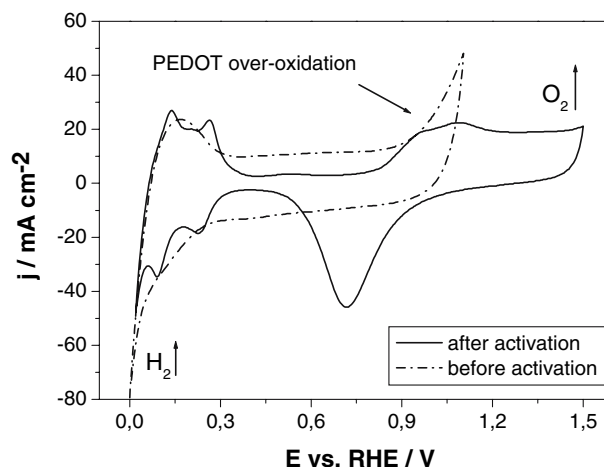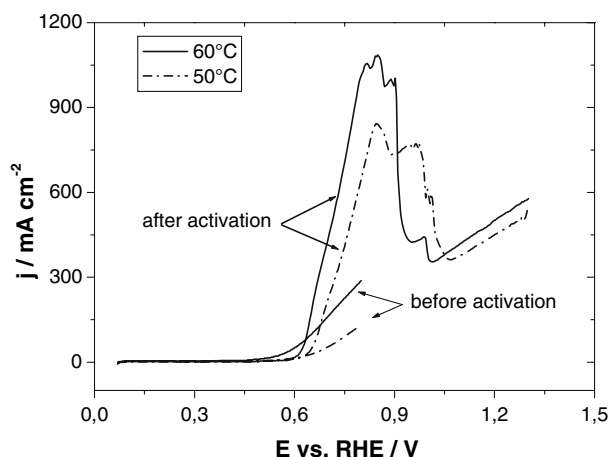

Fig. 1 Cyclic voltammograms of 1 mg cm^{-2} Pt-PEDOT/C in 1 M H_2SO_4 at 40 mV s^{-1} and room temperature

decreased to 0.1 mg cm^{-2}, which nearly corresponds to a decrease in reaction layer thickness by a factor of 10. Curve 2 in Fig. 4 shows the same poor activity of the non-
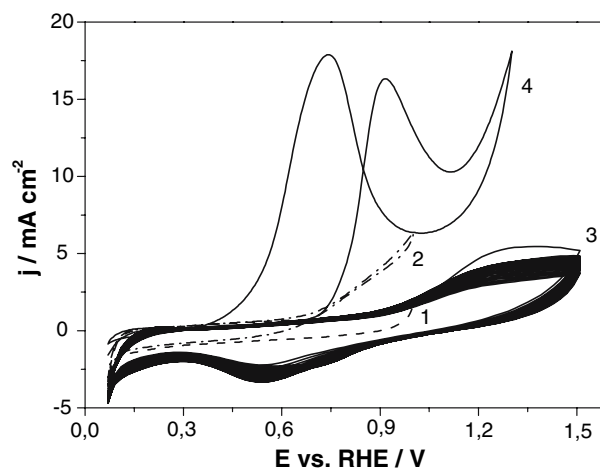
activated material for methanol oxidation, as described previously. After electrochemical activation in 1 M H$_2$SO$_4$ (curve 3), the current density of the methanol oxidation increased from 7 mA cm^{-2} (curve 2) to 17 mA cm^{-2} (curve 4).

The activity of PEDOT-based anodes for methanol oxidation was investigated in the DMFC. A power density of about 39 mW cm^{-2} was found for an electrochemically activated PEDOT-based MEA. This value was about twice that of a non-activated system. Interestingly, an enhancement of MEA performance was also observed with increasing storage time of the Pt-PEDOT/C anode, before its hot pressing with the membrane and cathode. The influence of the anode storage time on the DMFC performance is shown in Fig. 5 and compared with that of two Pt-VulcanXC72/C systems. The 2-week-old Pt-PEDOT/C-based MEA exhibited a power density of 36 mW cm^{-2}

Fig. 2 Cyclic voltammograms of (**a**) a fresh and (**b**) 1-month-old 1 mg cm^{-2} Pt-PEDOT/C in 1 M H$_2$SO$_4$ at 40 mV s^{-1} and room temperature

Fig. 4 Cyclic voltammograms of 0.1 mg cm^{-2} Pt-PEDOT/C in 1 M H$_2$SO$_4$ (1) before and (3) during electrochemical activation and in 1 M H$_2$SO$_4$ + 2 M CH$_3$OH (2) before and (4) after activation at 40 mV s^{-1} and room temperature

**Fig. 3** Linear sweep voltammograms of 1 mg cm^{-2} Pt-PEDOT/C in 1 M H$_2$SO$_4$ + 2 M CH$_3$OH at 40 mV s^{-1}
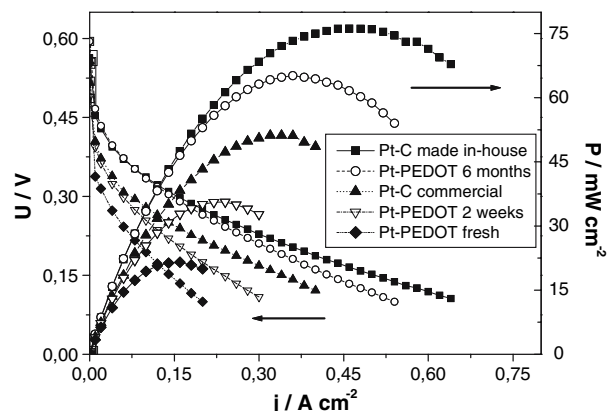
Fig. 5 U-j and P-j characteristics of different MEAs in 2 M CH$_3$OH at 2 bar methanol and oxygen back pressure and 80 °C

that is comparable with that of the electrochemical activated one (not shown in Fig. 5). A more spectacular enhancement of cell performance up to 65 mW cm^{-2} was obtained after 6-months' storage of the Pt-PEDOT/C electrode in air compared to that of the freshly prepared system (21 mW cm^{-2}). This value is even higher than that obtained with the commercial Pt-VulcanXC72/C system (50 mW cm^{-2}), but still lower than that measured at the Pt-VulcanXC72/C based MEA made in-house (75 mW cm^{-2}).

Figure 6 shows results of steady-state experiments of different MEAs at 200 mA cm^{-2} current density and 1.2 bar methanol and oxygen back pressure. The cell voltage of the 6-month-old Pt-PEDOT/C-based MEA was quite stable at about 200 mV and almost identical to that of the Pt-VulcanXC72/C system made in-house. However, at this high-current density, the cell voltage of the 2-week-old Pt-PEDOT/C-based MEA was unstable and decreased continuously.
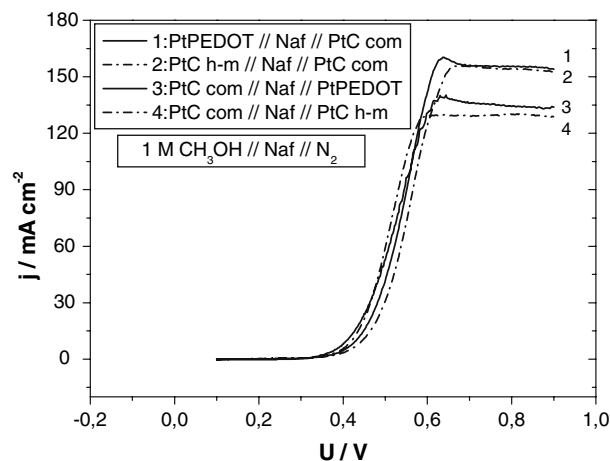
In order to get more insight into the methanol permeation within the MEA, the method proposed by Ren et al. [19] was used. Polarization of the fuel cell in electrolysis mode gives a good approximation of the methanol flux through the Nafion membrane after correction of the electro-osmotic drag. For this purpose, the cathode and the anode chambers are usually fed with a 1 M CH$_3$OH solution and an inert gas, respectively. In the case of VulcanXC72 based electrodes, the methanol oxidation rate at the anode is limited by the methanol diffusion through the Nafion membrane [19]. Since hydrogen evolution takes place in the cathode chamber filled with 1 M CH$_3$OH, it can be considered to behave approximately as a reference electrode. This method was applied in this work primarily to obtain some qualitative information about the influence of PEDOT degradation
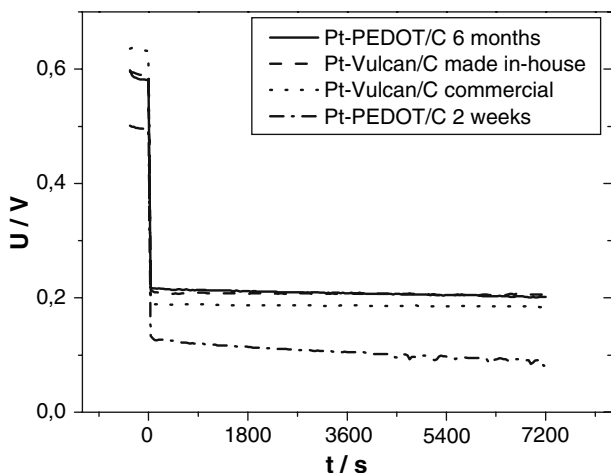
on methanol transport, catalyst activity and utilization. In the first step, the following MEAs were fabricated and tested as reference systems: "well-activated Pt-PEDOT//Nafion//Pt-Vulcan commercial" and a "Pt-Vulcan made in-house//Nafion//Pt-Vulcan commercial". In Fig. 7, curve 1 and 2 correspond to measurements in which Pt-PEDOT/C and Pt-VulcanXC72/C (made in-house) were in contact with the 1 M CH$_3$OH solution, while the methanol oxidation occurred at the commercial Pt-VulcanXC72 electrodes. The limiting current densities of the methanol oxidation at the commercial Pt–C electrodes (curves 1 and 2) were obviously determined by the methanol flux through the Nafion$^{®}$ 117 membrane and in good agreement with the data reported in [19]. It should be noted that the commercial Pt-VulcanXC72/C GDEs did not contain any Nafion in the reaction layer. In order to examine the methanol oxidation on the Pt-PEDOT/C and Pt-VulcanXC72 in-house made electrodes, the cell feed was inversed (curves 3 and 4). In this case, the methanol oxidation plateau was about 20 mA cm^{-2} lower (curves 3 and 4) than that of the commercial Pt–C electrodes (curves 1 and 2). This decrease of the limiting currents was obviously related to the presence of 10 wt.% Nafion in the in-house made Pt-PEDOT and Pt-VulcanXC72 reaction layers.

To study the time-dependence of Pt-PEDOT activity with respect to methanol oxidation and transport within the reaction layer, measurements were carried out in the electrolysis mode, for which results are illustrated in Fig. 8. In the case of the MEA with the freshly prepared electrode, the methanol oxidation occurred predominantly under ohmic control in the potential region between 550 and 850 mV. At higher potentials, the reaction became mass


Fig. 6 U-t characteristics of different MEAs at 200 mA cm^{-2}, 1.2 bar methanol and oxygen back pressure and 80 °C

Fig. 7 Linear sweep voltammograms (1–4) recorded in electrolysis mode with two different MEAs: "Pt-PEDOT//Nafion//Pt-C (commercial)" and "Pt-C (home-made)//Nafion//Pt-C (commercial)"; Curves 1 and 2 were obtained with Pt–C (com) in humidified N$_2$ feed, curves 3 and 4 after inverting the cell feeds. Sweep rate 1 mV s^{-1}; methanol and nitrogen back pressure 1.2 bar; 80 °C; start potential 100 mV

transport controlled. For the MEAs with the 2-week and 6-month-old Pt-PEDOT/C electrodes, the methanol oxidation reaction was primarily kinetically controlled. The limiting current density in the mass transport controlled region amounted to about 70 and 130 mA cm^{-2}, respectively. In the kinetically controlled region, the decrease in over-potential with storage time can be explained by a more efficient reactant and product diffusion through the reaction layer and a better utilization of the Pt catalyst. Changes in cell resistance were confirmed by impedance measurements (EIS) carried out in DMFC mode at 0.5 A and 1.5 bar methanol and oxygen pressure. The ohmic resistance, R_Ω, obtained from the intercept of the cell impedance with the real axes at high frequencies ($f \to \infty$), was found to be lower for MEAs with well-activated Pt-PEDOT/C anode. For example, values of R_Ω = 36, 40 and 95 mΩ were detected for MEAs with the 6-month-old, 2-week-old and freshly prepared anodes, respectively.

The influence of electrochemical activation and air storage on GDE morphology and composition was studied by means of Hg porosimetry and SEM/EDAX. The consequences of the appearance of additional nano-pores in the range of 3–10 nm are evident in the Hg porosimetry graphs, either after electrochemical over-oxidation of Pt-PEDOT (Fig. 9b) or more distinctly after its storage in air for 2 months (Fig. 9c). The calculated specific areas of the freshly prepared, electrochemically activated and 2-month-old Pt-PEDOT/C anode material were 1.042, 1.327 and 4.509 m^2 g^{-1}, respectively.

SEM/EDAX investigations were carried out at a Pt-PEDOT/C GDE with 10 wt.% Nafion and 20 wt.% PTFE as binder and hydrophobic material, respectively, at 1-month intervals. Changes in terms of particle morphology and layer porosity can be discerned on the SEM
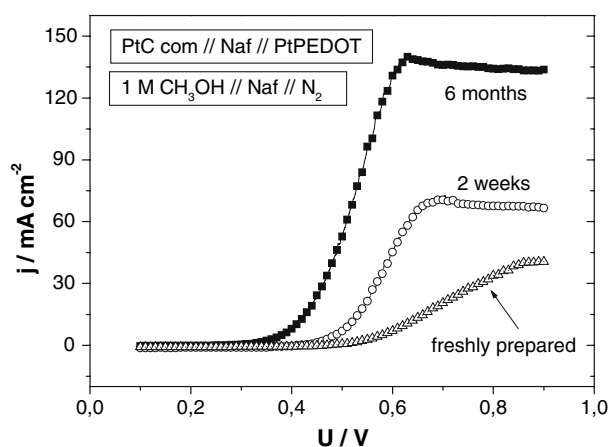
Fig. 8 Influence of the Pt-PEDOT storage time on methanol oxidation and transport behaviour in electrolysis mode. Sweep rate 1 mV s^{-1}, methanol and nitrogen back pressure 1.2 bar; 80 °C; start potential 100 mV
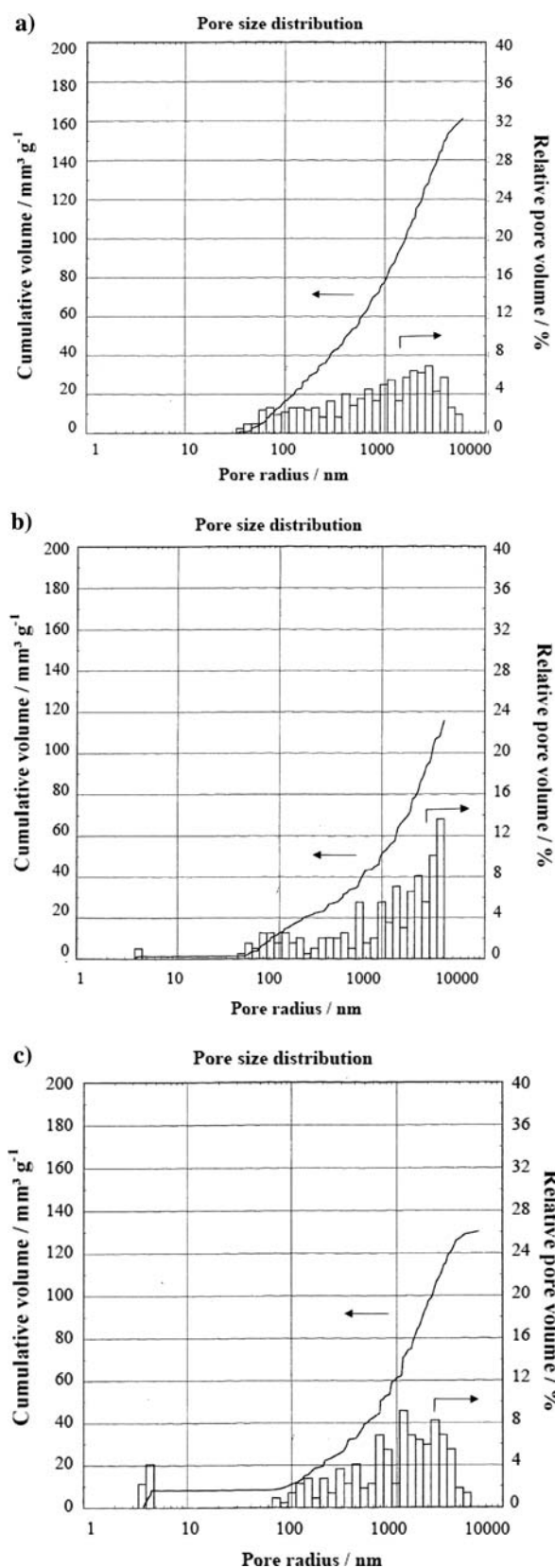
Fig. 9 Hg porosimetry graphs of (a) a freshly prepared, (b) an electrochemical activated and (c) a 2-month-old 1 mg cm^{-2} Pt-PE-DOT/C GDE

Fig. 10 SEM micrographs of (**a**) a freshly prepared 1 mg cm^{-2} Pt-PEDOT/C GDE, (**b**) after 1 month, (**c**) 2 months and (**d**) 3 months' storage in ambient air
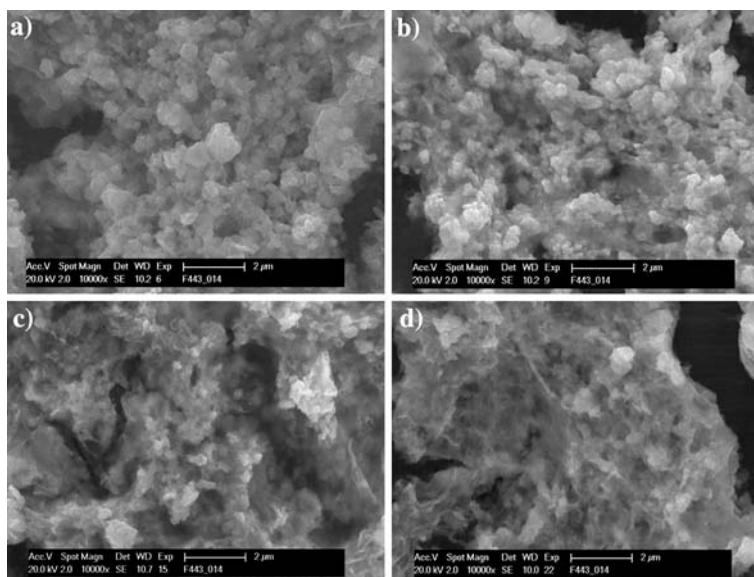

photomicrographs in Fig. 10. After 3 months' storage in air, the contour of most of the PEDOT particles in Fig. 10c vanished, while a continuous increase in porosity was evident in comparison with the freshly prepared sample. A weakening of O and S peak intensities was clearly identified in the EDX spectra. After 2 months, the amounts of O and S had already decreased by a factor two in comparison with their concentration in the freshly prepared material. Figure 11 shows comparative EDX spectra and elemental analysis of the same sample after 3 months' storage in air. No information about the decay of pure PEDOT under ambient air conditions was found in the literature; PEDOT is rather well known for its high degree of stability. EDX spectra of over 1-year-old PEDOT did not reveal any significant polymer alteration. However, a decrease in S signal intensity of about 30% was detected in an 8-month-old Pt-PEDOT powder. The polymer degradation process was obviously due to the high-Pt catalyst ratio and was probably accelerated by the high porosity of the GDE reaction layer, which offers a larger reaction surface to oxygen compared to that of a more agglomerated powder system. A similar degradation was observed by Lefebvre et al. [20] at a Pt-PEDOT-PSS system. The presence of Nafion and PTFE in our reaction layer may also have favoured PEDOT degradation.

4 Conclusion

The activity and long-term stability of PEDOT supported Pt catalyst were studied by means of electrochemical half-cell and fuel cell measurements, as well as SEM and Hg porosimetry. The conducting polymer PEDOT powder was prepared by chemical oxidation of the monomer EDOT with the oxidizing agent $Na_2S_2O_8$. Pt deposition on the

PEDOT substrate was carried out by chemical reduction of H_2PtCl_6 precursor in formaldehyde. The catalyst : substrate mass ratio and the Pt catalyst loading were fixed at 60:100
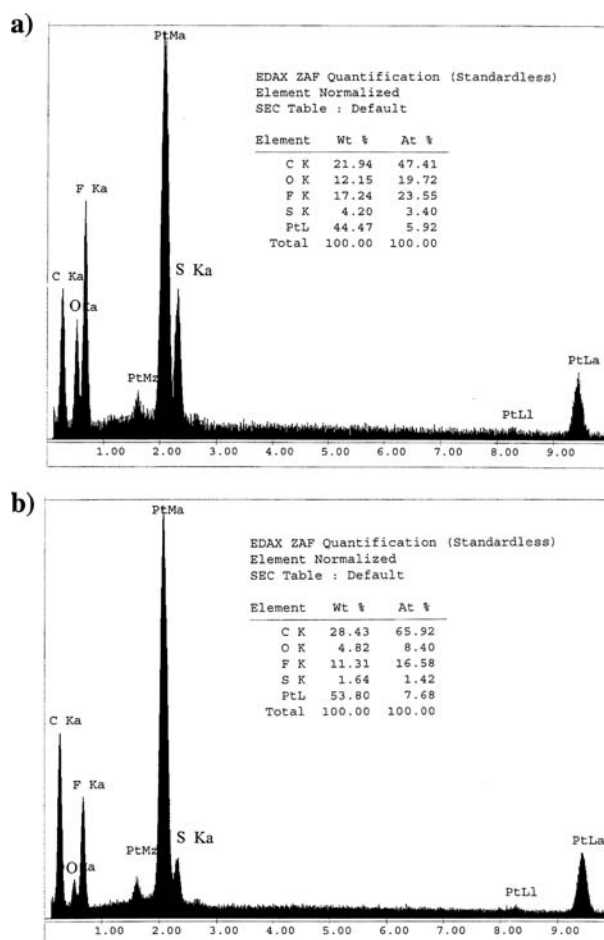
Fig. 11 EDAX spectra of (**a**) a freshly prepared 1 mg cm^{-2} Pt-PEDOT/C GDE, and (**b**) after 3 months' storage in ambient air

and 1 mg cm^{-2}, respectively. The 10 wt.% Nafion and 20 wt.% PTFE were incorporated into the catalyst ink, in order to optimize the sintering behaviour and hydrophobic properties of the reaction layer, respectively. Freshly prepared Pt-PEDOT/C GDEs showed poor activity for methanol oxidation. However, a clear improvement was observed after electrochemical over-oxidation or long-time storage of the Pt-PEDOT/C electrode in air. After 6-months' storage, the Pt-PEDOT/C performance in a DMFC was better than that of the electrochemically activated electrode and even close to that of Pt-VulcanXC72. This can be explained by the fact that both procedures led to a substantial depletion of S and O in the polymer matrix and furthermore to an increase in porosity of the reaction layer and methanol accessibility to the catalyst active centres. PEDOT degradation was obviously caused by the high-Pt loading and possibly by the presence of Nafion/PTFE and solvent residuals from the ink in the reaction layer. The enhancement of the specific area of Pt-PEDOT/C and the generation of additional nano-pores were also confirmed by Hg porosimetry measurements.

For the first time, the feasibility of PEDOT supported Pt catalyst as a DMFC anode material was demonstrated. However, after storage in air for several weeks, an impressive change in morphology was observed in the reaction layer, whereas PEDOT behaved more or less as a carbon precursor. Further investigations are still necessary to elucidate the mechanism of PEDOT degradation and to develop a more porous and chemically stable PEDOT-based reaction layer, with preserved mixed ionic and electronic conductivity.

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