

Short communication

# Sputter-deposited ultra-low catalyst loadings for PEM fuel cells

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## Abstract

Sputter-deposited Pt thin film layers are employed as catalyst material for polymer electrolyte membrane (PEM) fuel cells. An ultra-low catalyst loading of  $5 \mu\text{g cm}^{-2}$  platinum results in a maximum power density of  $124\text{--}132 \text{ mW cm}^{-2}$  depending on the gas diffusion layer substrate when feeding  $\text{H}_2/\text{O}_2$  at ambient temperature and pressure. By using the sputter deposition process less catalyst is needed for comparable cell performance to contemporary standard electrodes loaded with  $1 \text{ mg cm}^{-2}$  Pt that have been used for reference. Catalyst layers sputter-deposited onto different porous electrodes are investigated with respect to their effect on characteristic fuel cell performance which improves by 8% after adding chromium or palladium thin film layers.

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## 1. Introduction

The commercialization of fuel cells is still impeded by cost of materials and production. Many efforts are undertaken to reduce costs, e.g. lowering catalyst loadings, simplifying production processes, or modifying fuel cell designs. For PEM fuel cells operated at low temperature, high costs are due to the amount of platinum catalyst, which is not yet used efficiently.

Recent work is showing that low catalyst loadings sputtered on PEMs, e.g. below  $0.1 \text{ mg cm}^{-2}$ , allow to operate at yet remarkable power densities [1,2]. By repeatedly mixing sputtered Pt layers with layers of ionomer solution and carbon powder, the performance was further improved to  $320 \text{ mA cm}^{-2}$  at  $0.6 \text{ V}$  ( $60^\circ\text{C}$ ,  $\text{H}_2/\text{O}_2$ , 1 atm) at a Pt loading of only  $0.043 \text{ mg cm}^{-2}$  [1]. With direct sputtering of Pt to the anode and cathode gas diffusion layer (GDL), a similar performance of  $280 \text{ mA cm}^{-2}$  at  $0.6 \text{ V}$  ( $70^\circ\text{C}$ ,  $\text{H}_2/\text{air}$ , 1 atm) at a Pt loading of  $0.15 \text{ mg cm}^{-2}$  was achieved [3]. However, the performance of such fuel cells is mostly still falling behind that of conventional ink-based fuel cells with higher catalyst

loadings (usually  $\geq 0.4 \text{ mg cm}^{-2}$ ). Recently more than  $1200 \text{ mA cm}^{-2}$  at  $0.6 \text{ V}$  ( $85^\circ\text{C}$ ,  $\text{H}_2/\text{O}_2$ ,  $2/5 \text{ atm}$ ) at a Pt loading of  $0.4 \text{ mg cm}^{-2}$  were reported [4]. But also lower Pt loadings applied by special ink-based techniques are found to perform well, e.g.  $650 \text{ mA cm}^{-2}$  at  $0.6 \text{ V}$  ( $70^\circ\text{C}$ ,  $\text{H}_2/\text{O}_2$ , 1 atm) at  $0.1 \text{ mg cm}^{-2}$  Pt [5]. A similar result of  $520 \text{ mW cm}^{-2}$  maximum power density ( $35^\circ\text{C}$ ,  $\text{H}_2/\text{air}$ , 1 atm) with a cathode Pt loading of  $0.12 \text{ mg cm}^{-2}$ , but an anode Pt loading above  $1 \text{ mg cm}^{-2}$ , was reported more recently [6]. More results with different applied loadings to the anode and cathode side, sputtered and ink-based, have been shown to perform equally or better when operated at  $\geq 80^\circ\text{C}$  and elevated pressures [7–10].

As has been previously presented, miniaturized fuel cells can be fabricated by employing microsystem technology processes only, such as sputter deposition, plasma polymerization, and chemical vapor deposition, which allows an ultra-low catalyst loading by the sputter deposition process [11–13]. The catalyst material is applied to the electrode or PEM surface directly and the three-phase boundary (electrode–catalyst–PEM) is formed in a series of precise deposition processes avoiding any application of solution or ink containing arbitrarily distributed catalyst material, which causes the catalyst to be only partly in contact with the proton-

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conducting membrane or electrode and many catalyst sites to keep passive.

An additional advantage of the thin layer catalyst is that it is active in the immediate neighborhood to both the proton-conducting membrane and electrode. At high cell current densities and gas permeability limitations thick catalyst layers are only active closest to the gas supply, i.e. most distant from the proton-conducting membrane [8].

In this paper, the application of a catalyst sputter deposition process to standard electrodes and PEM materials is investigated.

## 2. Experimental

Platinum catalyst is sputter-deposited on two types of GDL, SIGRACET GDL-HM (SGL Technologies, SGL Carbon Group) and uncatalyzed ELAT (E-TEK Div., De Nora), which are subsequently referred to as SGL and E-TEK, respectively.

The thin layers of Pt were deposited from a Pt diode target at 50 W rf power and a pressure of 2 Pa at room temperature on the GDLs. The Pt loading is determined by the sputtering time and rate, i.e. by the measured Pt layer thickness deposited on a reference Si wafer sample per amount of time and the density of the material. Thus, all Pt film thicknesses on GDLs are nominal in the following and refer to its actual reference thickness as measured on Si wafers.

The GDLs and PEM were hot-bonded to form a membrane electrode assembly (MEA) at a temperature of 140 °C and a pressure of 290 kPa using a Nafion solution (5%, Sigma–Aldrich; applied to PEM at  $\leq 1.5 \text{ mg cm}^{-2}$  ionomer loading). For cleaning the PEM was rinsed in distilled water, ultrasonically assisted, for 15 min prior to the assembly. For all MEAs Nafion 115 (DuPont) membranes were used.

The sputtered catalyst thin layers were characterized by scanning electron microscopy (SEM) photographs (LEO 1530 Gemini, LEO Electron Microscopy), energy dispersive X-ray (EDX) analysis (Link ISIS 300, Oxford Instruments), and X-ray diffractometry (XRD) analysis (X'pert PRO, Philips).

Fig. 1 sketches the measuring chamber used for the MEA investigations. Single cells of  $2.25 \text{ cm}^2$  ( $15 \text{ mm} \times 15 \text{ mm}$  electrode area) are placed between the two metal plates with cavities and drilled in- and outlets at opposing ends for the fuel supply. Of the  $2.25$  only  $1.44 \text{ cm}^2$  are supplied by fuel via the cavity area. The peripheral area is compressed between the metal contact surrounding the chamber and an adjacent silicone gasket. The fuel, however, diffuses through the GDLs across the full area. A flow field design was not applied. A top view photograph of the lower half of the chamber is depicted in Fig. 2.

Oxygen and hydrogen are used as the reactants. All measurements are carried out at ambient pressure, 21 °C room temperature, a hydrogen flow of 20 sccm, and an oxygen flow of 4 sccm. Both reactants are slightly humidified by passing

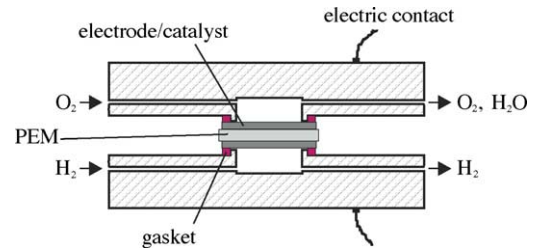


Fig. 1. Scheme of the employed fuel cell measuring chamber.

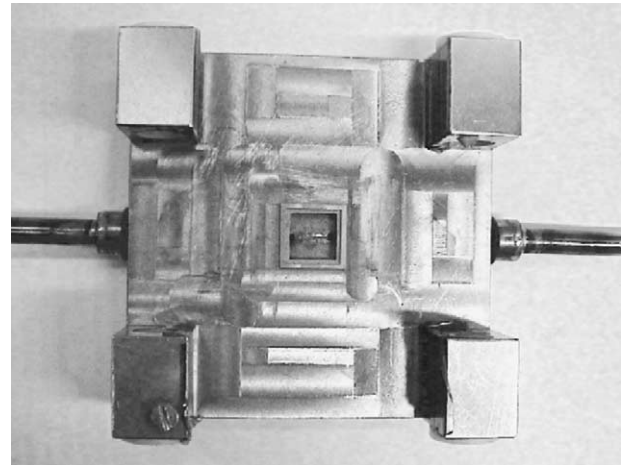


Fig. 2. Top view of the lower half of the fuel cell measuring chamber. Reactants enter through the pipe from the left and exit to the right. The single cell MEA is placed over the cavity ( $12 \text{ mm} \times 12 \text{ mm}$ ) shown in the center of the photograph.

them through water-containing glass cylinders at room temperature.

For each presented data point a minimum of two samples have been prepared and measured. The load is simulated by applying a potential to a resistance in parallel to the fuel cell or by applying an inverse current to the fuel cell itself. Both techniques are controlled by a PC system that collects the data from a set of data acquisition units (Agilent Technologies).

## 3. Results and discussion

### 3.1. Sputtered platinum thin layers

The thin film growth of sputter-deposited Pt was characterized by XRD measurements and SEM photographs.

A representative example for the XRD spectra for the thin films sputter-deposited at constant process parameters pressure, flow, temperature, and power is shown in Fig. 3. It exhibits a significant peak representing the (1 1 1) reflection of Pt. Furthermore the Pt peak of the (2 2 2) orientation can be seen. No further orientations are present indicating a perfectly oriented crystallographic texture of the grown platinum. Calculations and experiments agree that low energy paths for the dissociation of molecular hydrogen result from the Pt(1 1 1) surfaces [14].

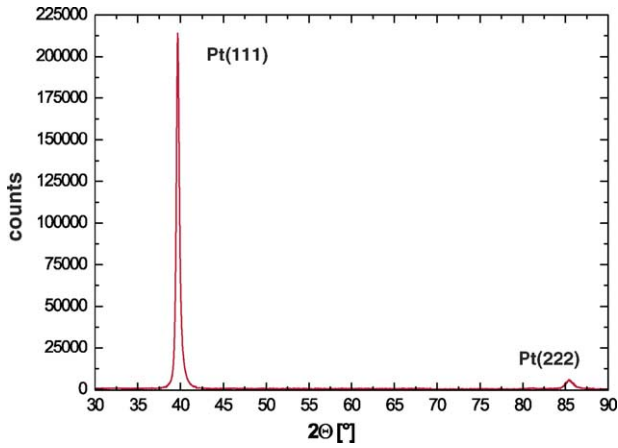


Fig. 3. XRD pattern of a 440 nm Pt thin film sample. Pt sputter-deposited at ambient temperature, 50 W rf power, and 2 Pa.

In Fig. 4, SEM photographs of the SGL substrate covered with Pt thin films of 10, 20, 50, 100, 200, and 500 nm thickness are shown. The sample covered with 10 nm Pt has only a layer of very few atoms of the catalyst, which are mostly congregated and grow in small islands. The structure of the original substrate (not shown) is still evident. As the Pt layer thickness increases, the catalyst coverage of the GDLs as well as the smoothness increases. More and more micropores of the GDL narrow and are even completely closed. At a Pt layer of 500 nm, only pores of larger diameter remain open.

Fig. 5 shows EDX line scans for Pt of two different SGL samples. The upper one is of a sample with 5 nm of Pt, the lower half shows a sample loaded with 25 nm. Next to the higher amount of counts along the scanned line (362.9 μm at 7092 frames each), which is in accordance with the Pt loading, the roughness of the samples decreases with increased

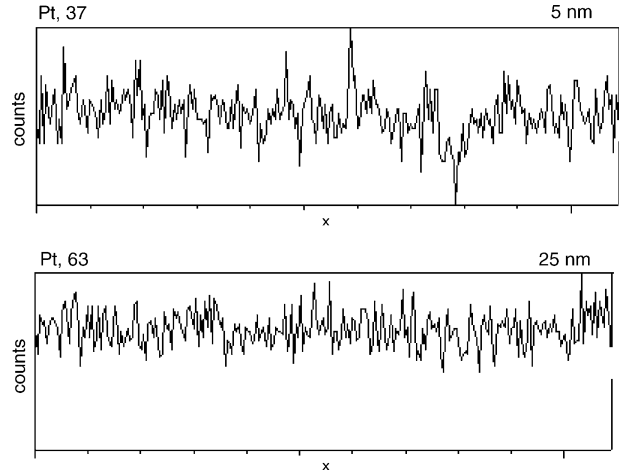


Fig. 5. EDX line scans for platinum of SGL samples with a 5 nm Pt layer (upper half) and a 25 nm Pt layer (lower half).

catalyst thickness. This has also been visible from the SEM photographs of Fig. 4, as smaller pores are starting to be completely covered by the sputtered catalyst layer with increasing layer thickness. However, due to the underlying substrate surface morphology and the energy-driven Pt growth starting from islands of sputtered atoms, surface roughness initially increases and later decreases to resemble the original sample structure as an evenly deposited Pt film spreads out.

### 3.2. Fuel cell performance measurements

Films of identical thickness were sputter-deposited on the GDLs for anode and cathode of a MEA, i.e. both bear identical platinum loading for each measurement.

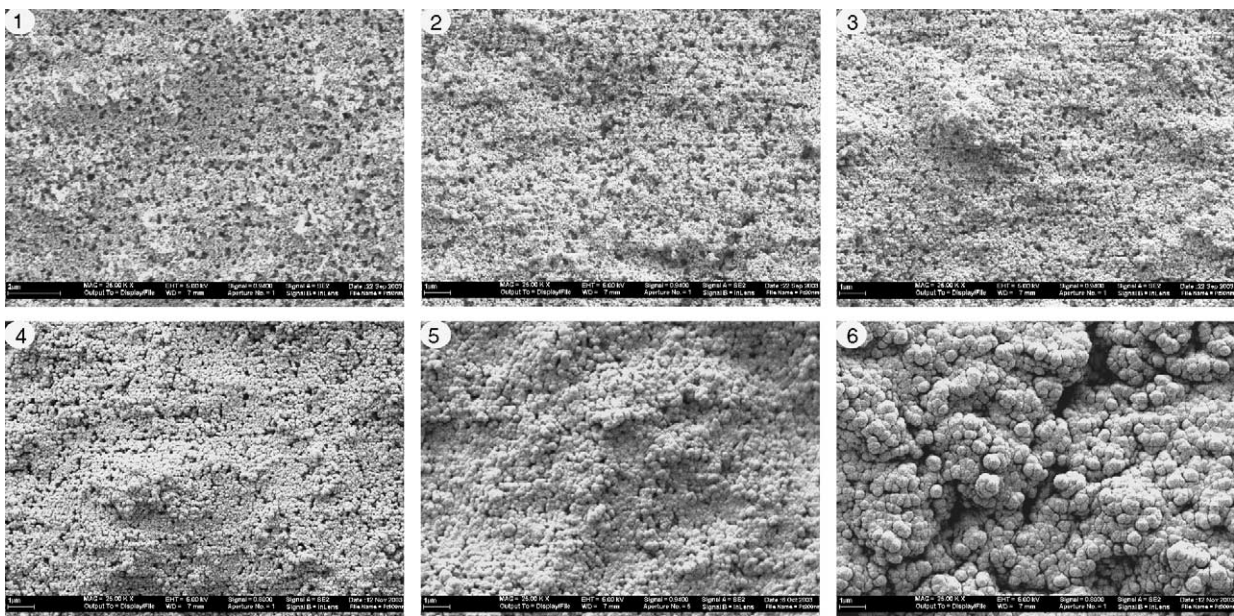


Fig. 4. SEM photographs of SGL gas diffusion layers with Pt thin films of (1) 10 nm, (2) 20 nm, (3) 50 nm, (4) 100 nm, (5) 200 nm, and (6) 500 nm thickness.



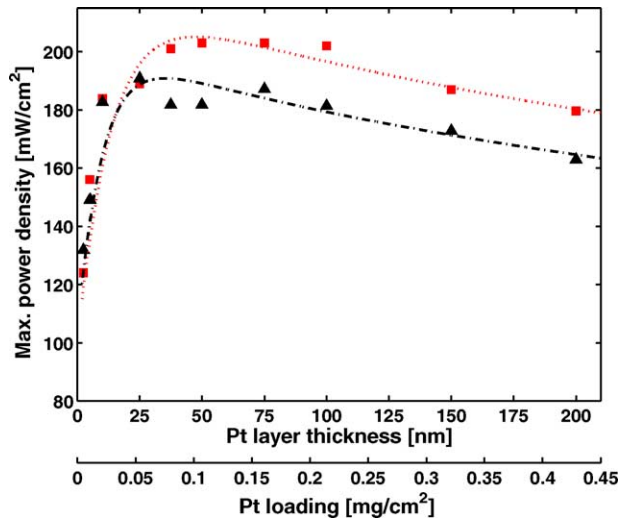


Fig. 6. Maximum power density vs. Pt layer thickness on E-TEK (■) and SGL (▲) electrodes ( $21^\circ\text{C}$ , ambient pressure, and  $\text{H}_2/\text{O}_2$  operation).

The graph in Fig. 6 displays the maximum power density versus Pt thickness of SGL and E-TEK samples between 0 and 200 nm, i.e. a platinum loading of  $0\text{--}0.429\text{ mg cm}^{-2}$ . Only a slight difference in performance between the SGL and E-TEK samples is observed. Up to loadings of  $0.054\text{ mg cm}^{-2}$  (25 nm), samples prepared from both substrates perform almost alike. At higher loadings the E-TEK samples outperform the fuel cells prepared with SGL electrodes by approximately 10%. This may be due to the difference in microporous coating of the E-TEK as compared to the SGL samples. E-TEK samples might be better suited for the sputter deposition technique at high loading due to their micropore sizes and trenches of larger scale. In contrast SGL samples perform more effectively at low catalyst loadings ( $\leq 0.054\text{ mg cm}^{-2}$ ). It has to be noted that these slight differences may vary with the production lot or its transport and handling prior to the assembly, respectively. MEAs investigated here were all prepared from one GDL lot of E-TEK and SGL. Due to this similarity in pore size and structural quality, no drastic differences in performance for the two investigated GDLs with sputtered Pt loadings were observed.

The maximum power density achieved with a Pt layer thickness of 2.5 nm ( $0.005\text{ mg cm}^{-2}$ ) was  $124\text{ mW cm}^{-2}$  for E-TEK and  $132\text{ mW cm}^{-2}$  for SGL, respectively. At 5 nm ( $0.011\text{ mg cm}^{-2}$ ) Pt,  $156\text{ mW cm}^{-2}$  were observed for E-TEK compared to  $149\text{ mW cm}^{-2}$  for SGL. For catalyst layer thicknesses of 10 and 25 nm the results for both GDL substrates are almost equal at about 184 and  $191\text{ mW cm}^{-2}$ , respectively.

The best performance for SGL samples was obtained at a Pt loading of  $0.054\text{ mg cm}^{-2}$  ( $191\text{ mW cm}^{-2}$ ,  $285\text{ mA cm}^{-2}$  at 0.6 V) and at  $0.107\text{ mg cm}^{-2}$  for E-TEK ( $203\text{ mW cm}^{-2}$ ,  $301\text{ mA cm}^{-2}$  at 0.6 V).

Fig. 7 depicts the maximum power density achieved for SGL GDLs with Pt loadings of up to  $3.218\text{ mg cm}^{-2}$ . Sputtered Pt loadings of more than  $0.1\text{--}0.2\text{ mg cm}^{-2}$  do not

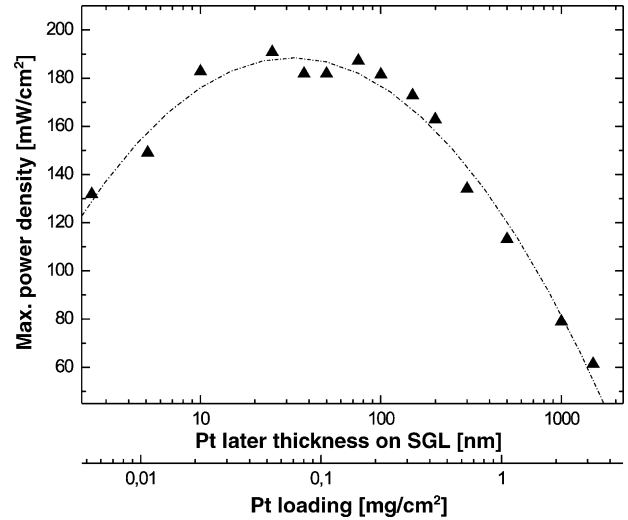


Fig. 7. Power density vs. Pt layer thickness on SGL (▲) electrodes ( $21^\circ\text{C}$ , ambient pressure, and  $\text{H}_2/\text{O}_2$  operation).

further improve fuel cell performance. At thicker Pt layers only pores of large diameter keep open for the fuel supply and these thick sputtered layers become more dense. That is limiting the water transport as only few pores remain. This results in a higher resistance and lower electrochemically active surface area of the sputtered catalyst. In addition the reduced activity in a thicker catalyst layer widens the gap between proton-conducting membrane and gas supply. This may also decrease cell voltage at higher current densities.

The measured current densities at 0.6 V and the open circuit voltages for the E-TEK are shown in Fig. 8. When plotting the resulting power per amount of Pt-loading versus the current density (Fig. 9), it becomes obvious that the fuel cells with thin sputtered catalyst films are highly efficient with respect to power yield per catalyst amount. Cells with a sputter-deposited Pt loading of  $0.005\text{ mg cm}^{-2}$  are by two orders of magnitude more efficient in platinum utilization

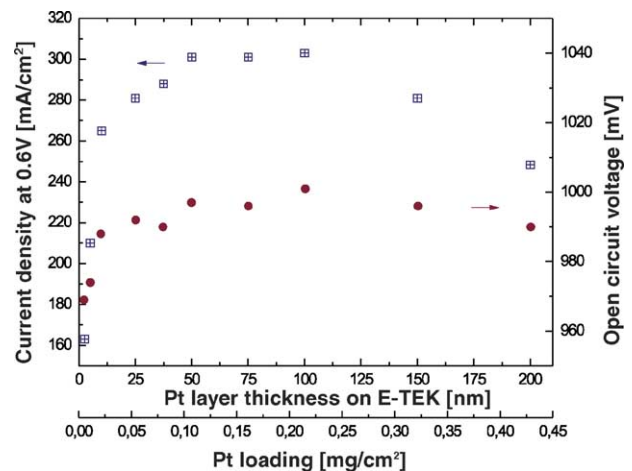


Fig. 8. Variation of current density at 0.6 V (□) and open circuit voltage (●) with Pt layer thickness on E-TEK electrodes ( $21^\circ\text{C}$ , ambient pressure, and  $\text{H}_2/\text{O}_2$  operation).

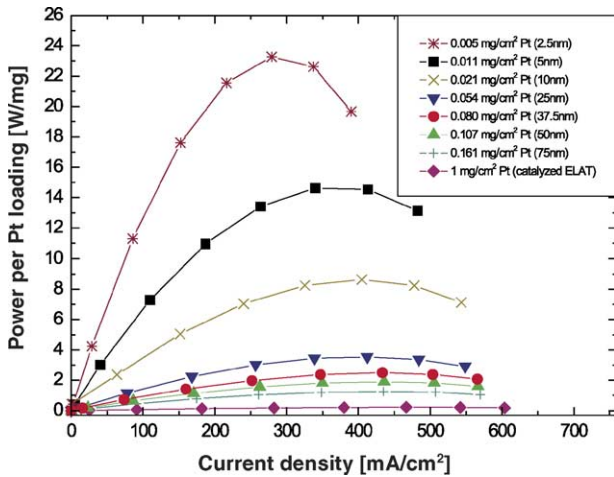


Fig. 9. Power per mg Pt amount vs. current density for different Pt loadings on E-TEK (21 °C, ambient pressure, and H<sub>2</sub>/O<sub>2</sub> operation).

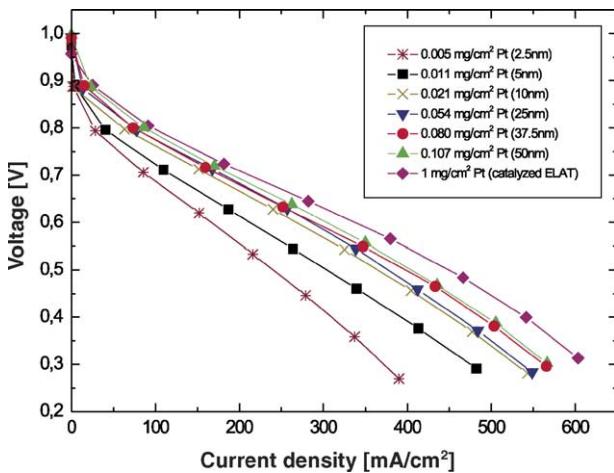


Fig. 10. Current–voltage plots for various amounts of sputtered Pt loadings on E-TEK and one sample using catalyzed ELAT containing 1 mg cm<sup>-2</sup> Pt. All measurements were carried out feeding H<sub>2</sub>/O<sub>2</sub> at room temperature and ambient pressure.

compared to the samples prepared from standard (non-sputtered) catalyzed ELAT loaded with 1 mg cm<sup>-2</sup>. It should be noted, however, that it takes significantly longer time for such a low loaded MEA to reach its optimum performance, as product water permeates from only few spots to wet the ion-conducting membrane, if the fuels are not humidified.

Fig. 10 illustrates that the cell with catalyzed ELAT, which was prepared for reference, outperforms (225 mW cm<sup>-2</sup>) the

Table 1  
Maximum power density for MEAs prepared with 25 nm Pt (0.054 mg cm<sup>-2</sup>) on E-TEK GDLs and inserted Cr, Pd, or Nafion solution layers of different thicknesses

| Inserted layer                               | None | Cr  | Cr  | Pd  | Pd  | Nafion |
|--|------|-----|-----|-----|-----|--------|
| Thickness (nm)                               | –    | 2×1 | 2×4 | 15  | 47  | ≥1500  |
| Maximum power density (mW cm <sup>-2</sup> ) | 189  | 200 | 183 | 201 | 203 | 164    |

As for all previous samples, anode and cathode electrodes are identical.

sputter-deposited one. However, this difference is small and e.g. just 12% for the E-TEK sample loaded with one order of magnitude less catalyst (0.08 mg cm<sup>-2</sup> Pt, 201 mW cm<sup>-2</sup>). From the lower open circuit voltage (Fig. 8) and this graph it can be concluded that catalyst loadings below 0.01 mg cm<sup>-2</sup> Pt do not provide sufficient catalytic sites for an efficient fuel cell performance on the GDLs considered here.

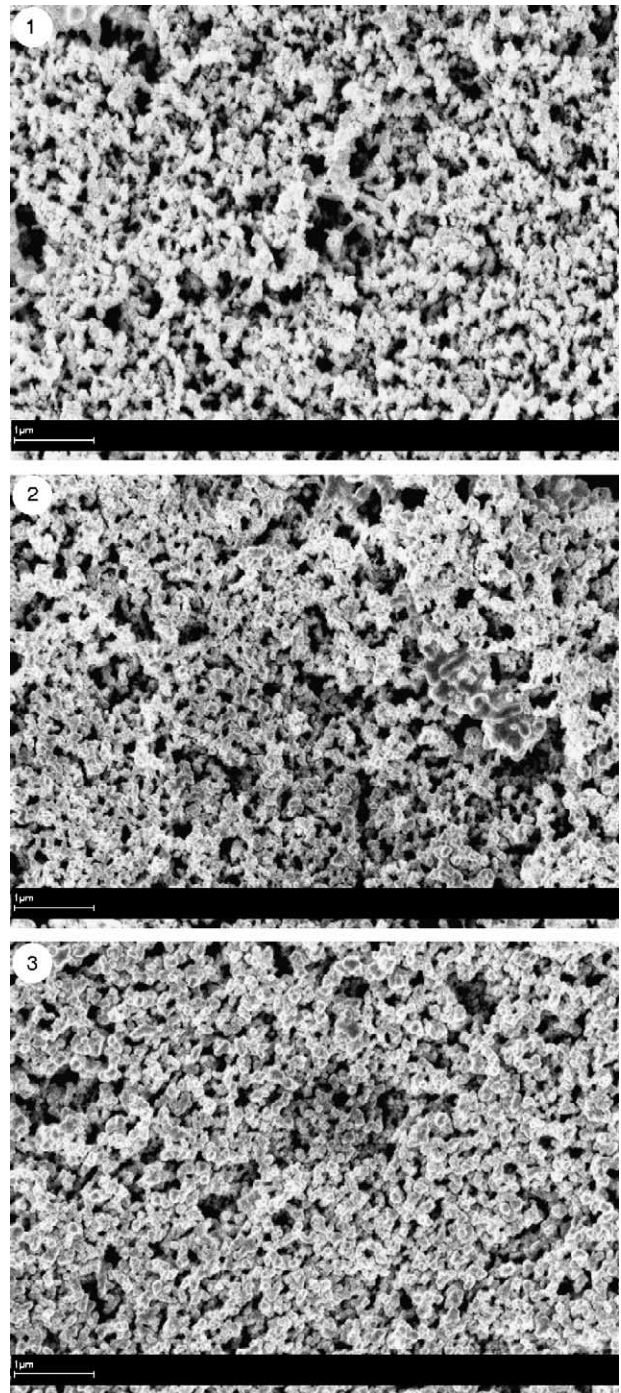


Fig. 11. SEM photographs of E-TEK with a 16 nm Pt thin film and (1) no Cr, (2) two 1 nm layers of Cr, and (3) two 4 nm layers of Cr inserted.

In order to investigate whether the performance of the fuel cells can be improved by altering the morphology of the catalyst sites the sputter process for the 25 nm Pt layer on E-TEK was split into several steps and additional layers were introduced beneath or between the Pt. Sputtering the 25 nm of platinum on vapor-deposited 47 nm thick Pd layer increased the maximum performance of the fuel cell to  $203 \text{ mW cm}^{-2}$ . Inserting two sputter-deposited 1 nm thin layers of Cr into the 25 nm Pt thin film resulted in an improvement of about 6%. Details are listed in Table 1.

SEM photographs of a 15 and 47 nm Pd film on E-TEK evidenced that even at a thin film thickness of 47 nm Pd a still highly porous layer evolved. Any potential diffusion resistance for the oxygen arising at this layer thickness is outweighed by an improvement in electric conductivity by the Pd.

By the insertion of Cr the succeeding sputtered Pt layer on Cr does not necessarily start to grow on present Pt atoms but finds alternative places of minimum energy on the GDL substrate surface. This yields in the observed higher efficiency as the platinum catalyst is more dispersed across the surface and more catalytically active sites are available. Addition of a Cr top layer on Pt does not improve the performance, i.e. Cr itself is not catalytically active. It is only effective if applied below or in the Pt thin layer, where it changes the layer morphology. From the SEM photographs in Fig. 11 it can be derived that the insertion of 4 nm Cr layers causes a denser morphology compared to the one with 1 nm inserted. For this reason the performance of fuel cells with 4 nm of Cr inserted does not improve compared to the sample with bare Pt. Investigations with spray-coated Nafion films (5% Nafion solution, Sigma-Aldrich) inserted into the Pt thin layer clearly diminished the fuel cell performance. This is attributed to the rather high thickness of the spray-coated Nafion films, which decreases the electric conductivity in the catalyst layer, the diffusivity of the fuel and, hence, the fuel cell performance.

Further investigations regarding these results, especially the use of Pd or other known to be hydrogen permeable materials as an addition to the anode GDL/catalyst for enhancing fuel cell performance, seem promising and are currently in progress.

#### 4. Conclusion

The objective of this work was to demonstrate that sputter-deposited Pt catalyst layers cannot only be used in miniaturized thin film fuel cells, but also allow to lower the catalyst loading for cells prepared by standard fabrication techniques. The optimum amount and distribution of sputtered Pt on representative GDLs was evaluated.

Although the cell performance of GDLs with sputter-deposited Pt layers were not as good as with catalyzed ELAT

electrodes of  $1 \text{ mg cm}^{-2}$  Pt loading, they only fell about 10% short at a catalyst loading of one order of magnitude less.

With a loading of only  $0.005 \text{ mg cm}^{-2}$  of sputtered Pt on E-TEK ( $124 \text{ mW cm}^{-2}$ ) more than 60% of the optimum maximum power density was attained compared to a 20-fold loaded one of  $0.107 \text{ mg cm}^{-2}$  ( $203 \text{ mW cm}^{-2}$ ), i.e. such a low loading can already be sufficient for low power, low cost applications as, e.g. low energy consuming microsystems and sensors.

Evidently, the layer density of the sputter-deposited Pt growing with thickness limits the performance. This may be avoided by applying additional materials to the Pt to modify the seeding and morphology. The inclusion of thin layers of Cr for example showed that the fuel cell performance can be improved. Two ultra-thin Cr layers introduced into a 25 nm Pt catalyst layer ( $0.054 \text{ mg cm}^{-2}$ ) improved the performance to  $200 \text{ mW cm}^{-2}$  corresponding to the maximum power density gained at twice the Pt loading.

Based on these results, further experiments to improve the performance of sputtered catalyst thin layers, e.g. by adding thin hydrogen permeable materials (Pd or silicone) between the GDL anode and the catalyst to increase the number of catalyst sites accessible for the fuel, are under investigation.

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#### References

- [1] S.Y. Cha, W.M. Lee, *J. Electrochem. Soc.* 146 (1999) 4055–4060.
- [2] R. O'Hayre, S.-J. Lee, S.-W. Cha, F.B. Prinz, *J. Power Sources* 109 (2002) 483–493.
- [3] A.T. Haug, R.E. White, J.W. Weidner, W. Huang, S. Shi, T. Stoner, N. Rana, *J. Electrochem. Soc.* 149 (2002) A280–A287.
- [4] E. Antolini, R.R. Passos, E.A. Ticianelli, *J. Power Sources* 109 (2002) 477–482.
- [5] Y.-G. Chun, C.-S. Kim, D.-H. Peck, D.-R. Shin, *J. Power Sources* 71 (1998) 174–178.
- [6] Z. Qi, A. Kaufman, *J. Power Sources* 113 (2003) 37–43.
- [7] S. Hirano, J. Kim, S. Srinivasan, *Electrochim. Acta* 42 (1997) 1587–1593.
- [8] M.S. Wilson, S. Gottesfeld, *J. Appl. Electrochem.* 22 (1992) 1–7.
- [9] M.S. Wilson, S. Gottesfeld, *J. Electrochem. Soc.* 139 (1992) L28–L30.
- [10] H.A. Gasteiger, J.E. Panels, S.G. Yan, *J. Power Sources* 127 (2004) 162–171.
- [11] L. Mex, J. Müller, *Membr. Technol.* 115 (1999) 5–9.
- [12] L. Mex, M. Sussiek, J. Müller, *Chem. Eng. Commun.* 190 (2003) 1085–1095.
- [13] L. Mex, N. Ponath, J. Müller, *Fuel Cells Bull.* 39 (2001) 9–12.
- [14] R.A. Olsen, G.J. Kroes, E.J. Baerends, *J. Chem. Phys.* 111 (1999) 11155–11163.