ABSTRACT

DMFC cathode catalyst layers as part of MEA’s are prepared by pulsed electro-deposition (PED). A mixture of hexachloroplatinic acid dissolved in Nafion solution and carbon Vulcan XC 72 is used as a precursor and the platinum particles are deposited in the Nafion/carbon interface. The deposition is optimized by varying the pulsing parameters: pulse current density (j_pulse), pulse duration (t_on) and pulse interval duration (t_off). In dependence on the pulsing conditions, the performance of the electro-deposited catalyst layers differs by more than one order of magnitude. The best cathode performance is obtained at high pulse current density and low ‘on’- and ‘off-time’ (j_pulse = 1000 mA/cm², t_on = 2 ms, t_off = 10 ms). A second maximum is obtained at low current density and high ‘on’- and ‘off-time’ (j_pulse = 100 mA/cm², t_on = 200 ms, t_off = 500 ms). In comparison with commercial platinum catalyst (E-TeK), the size of the electro-deposited catalyst particles is three times larger (about 11 nm) and thus the platinum surface accordingly smaller, but the utilization is probably 3-4 times higher. As a result, the average performance of both catalysts is similar. If the size of the electro-deposited platinum particles can be reduced by further optimization of the PED process, an improvement of the cathode performance by a factor of three is expected.

INTRODUCTION

A disadvantage of commercial fuel cell electrodes prepared by common preparation techniques is the low catalyst utilization [1,9]. This is caused by a considerable amount of the catalyst, which is not in direct contact with the ionomer phase and therefore is unable to contribute to electrochemical reactions. Consequently, a substantial reduction of the catalyst loading can be realized by preparing the catalyst particles in the ionomer/carbon interface. This goal can be achieved by electrochemical deposition of the catalyst particles by using plating baths containing a soluble noble metal salt (see e.g. [2,3]).

We have developed a new preparation method [12], where in the first step, a precursor layer is fabricated by spraying a suspension of the soluble catalyst salt dissolved in a Nafion solution and carbon particles, which is either the Nafion membrane or the backing layer. In the second step, the catalyst particles are deposited onto the carbon particles by
pulsed electro-deposition [4,5]. This method allows to control the size of the crystallites depending on the deposition parameters.

In the present work, we have prepared platinum catalyst layers by pulsed electro-deposition. These catalyst layers are part of DMFC cathodes in MEA's with an electrode area of about 2 cm². The deposition was optimized by varying the pulsing parameters, i.e. pulsed current density, pulse duration ('ton') and pulse interval duration ('toff'). The optimum pulsing conditions are obtained by means of a statistical method.

**EXPERIMENTAL**

**Preparation of MEA's / electrode geometry and compositions:**

At first, anode catalyst layers are prepared by spraying a mixture of unsupported Pt/Ru (1:1) black (Johnson Matthey), an appropriate amount of 15 % Nafion solution (Ion Power, Inc.) and isopropanol onto a backing layer made of 60 wt% carbon black (XC 72) and 40 wt% PTFE (Dyneon GmbH, TF 5032) supported by carbon cloth (E-Tek, Inc., “A” cloth). The catalyst loading was about 4 mg/cm². The disk-shaped anodes are hotpressed (T = 130 °C, p = 0.5 kN/cm²) onto a Nafion 117 membrane. They have an electrode area of 1.8 cm² and act as a counter electrode. Half cell measurements can be performed by means of a ring-shaped reference electrode with the same composition as the counter electrode.

In the second step, precursor layers of the cathode catalyst layers are fabricated by spraying a suspension of solubilized Nafion (15 %, Ion Power, Inc.), carbon support (Vulcan XC72) and hexachloroplatinic acid as soluble catalyst salt homogeneously dispersed in i-propanol on the opposite side of the Nafion membrane. The geometry and size of the precursor layer is alike the counter electrode. The precursor layer is baked in an oven until dry. The composition of the precursor layer is adjusted in such way, that after the electro-deposition, the catalyst layer consists of 10 wt% Nafion and 90 wt% carbon supported catalyst. The latter consists of 40 wt% platinum and 60 wt% carbon Vulcan XC72. The amount of hexachloroplatinic acid corresponds to a platinum loading of about 0.5 mg/cm².

Finally, the platinum(IV) ions in the Nafion phase of the MEA cathode precursor layer are electrochemically reduced by formation of platinum catalyst particles. The pulsed electrochemical deposition is carried out in a thermostated vessel, which is schematically shown in Fig.1. The vessel is partially filled with water, which is kept at a temperature of 40 °C and purged with nitrogen. The MEA is placed in the upper part of the vessel with the precursor cathode layer on top. On the one hand, this arrangement avoids contact of the precursor layer with liquid water and a subsequent leaching of the platinum salt. On the other hand, the water vapor ensures a sufficient swelling and thus proton conductivity of the Nafion phase. The pulsed electrochemical deposition of platinum is performed by applying an appropriate current between the cathode (precursor layer) and the anode (counter electrode). For this purpose, negative rectangular voltage pulses are generated by a Wavetek Model 39 Generator. These voltage pulses are transformed into current pulses and amplified by a Kepco Bipolar Operational Power Supply (BOP 20-10M), with a maximum output current of 20 A. The resulting voltage pulses are recorded by a
Tektronix TDS 3012 B oscilloscope. A scheme of the pulsing process and the electrochemical reaction are shown in Fig.2. The overall charge during each pulsing process was set five times higher than the theoretical charge calculated from Faraday's law, to avoid incomplete reduction of the platinum salt caused by capacitive effects and side reactions like hydrogen evolution. Thus, the pulsing period was five times longer than the calculated value and ranged from 5 seconds (Exp. No.9) to 4 hours (Exp. No.2), depending on the pulsing conditions. The complete reduction of the platinum was proved by elementary analysis. The pulsing parameters used for the PED process are described in the next section.

**Experimental Design:**

The optimization of the pulsed electrochemical deposition was achieved by means of a factorial $2^3$ experimental design using the STATGRAPHICS® Software (Umex GmbH, Dresden, Germany). The factorial $2^3$ experimental design demands a variation of three parameters, here: a. pulsed current density, b. pulse duration (‘ton’), c. pulse interval duration (‘toff’). For each of these parameters, two values, i.e. a lower value and a higher value, are defined (see table 1). Therefore, $2^3 = 8$ experiments have to be performed. Additionally, a measurement of the centerpoint is useful to check the linearity of the system within the limits of variation. Hence, nine parameter combinations were investigated, as listed in table 2.

**Table 1: Variation of the pulsing parameters**

| parameter       | lower value | higher value | medium value |
|-----------------|-------------|--------------|--------------|
| $j_{\text{pulsed}}$ / mA * cm$^{-2}$ | 100         | 1000         | 550          |
| $t_{\text{on}}$ / ms                      | 2           | 200          | 101          |
| $t_{\text{off}}$ / ms                     | 10          | 500          | 255          |

**Table 2: Factorial $2^3$ experimental design for the optimization of the pulsing parameters**

| Experiment No. | $j_{\text{pulsed}}$ / mA * cm$^{-2}$ | $t_{\text{on}}$ / ms | $t_{\text{off}}$ / ms |
|----------------|--------------------------------------|-----------------------|-----------------------|
| 1 (centerpoint) | 550                                  | 101                   | 255                   |
| 2              | 100                                  | 2                     | 500                   |
| 3              | 100                                  | 200                   | 500                   |
| 4              | 100                                  | 2                     | 10                    |
| 5              | 1000                                 | 2                     | 500                   |
| 6              | 100                                  | 200                   | 10                    |
| 7              | 1000                                 | 200                   | 500                   |
| 8              | 1000                                 | 2                     | 10                    |
| 9              | 1000                                 | 200                   | 10                    |

The platinum catalyst layers prepared with the nine pulsing parameter combinations were characterized by quasi-stationary current potential measurements of oxygen reduction. In order to obtain reliable results, three samples were prepared and characterized for each of the nine parameter combinations.
Electrochemical characterization:

The performance of the cathodes prepared by PED was characterized by quasi-stationary current/potential measurements of oxygen reduction (scan rate: 20 mV/s) and impedance spectroscopy ($U = 10 \text{ mV}$). All the electrochemical measurements were performed with a three electrode arrangement. The electrode potential, $U (\text{RE})$, is measured vs. the reference potential of the methanol reaction established at the anode ring. Because the platinum loading of the cathodes is slightly different (0.4 – 0.6 mg/cm²), the current density is normalized to the platinum loading. A more detailed description of the electrochemical apparatus as well as the geometry of the MEA's and the measuring cell is to be found in /10/.

RESULTS AND DISCUSSION

Fig. 3 shows current/potential curves of oxygen reduction on DMFC cathodes prepared by the nine different pulsing conditions described in the experimental section. It is evident from these curves, that the performance of the cathodes is strongly affected by the pulsing conditions. The highest current densities reached with pulsing condition No. 8 ($j_{\text{pul}} = 1000 \text{ mA/cm}^2$, $t_{\text{on}} = 2 \text{ ms, } t_{\text{off}} = 10 \text{ ms}$) are about one order of magnitude higher than the current densities e.g. obtained with pulsing condition No. 5 ($j_{\text{pul}} = 1000 \text{ mA/cm}^2$, $t_{\text{on}} = 2 \text{ ms, } t_{\text{off}} = 500 \text{ ms}$). It should be stressed, that because of the methanol permeation through the Nation membrane, the cathode potential is rather a mixed potential with a dominating oxygen reduction than the overpotential of oxygen reduction. The combination of methanol permeation and the small platinum loading of the cathode induces relatively low potentials. In some cases, steep current/potential curves (see e.g. Exp. No 8 !) are obtained, which may be interpreted by a decreasing methanol permeation with rising current density. As a result, the mixed potential shifts to more positive values and the current/potential curve seems to be 'overcorrected'.

As mentioned in the experimental section, the experiments shown in Fig. 3 were repeated twice with new samples. The resulting three blocks of experimental data were analyzed by using the STATGRAPHICS® Software. The goal of this analysis is to find the optimum pulsing conditions in the parameter field investigated. More precisely, it means to search for the highest current density of oxygen reduction at a constant cathode potential. We have committed a cathode potential of 0.4 V as a representative value. In Figs.4-6, the calculated current density of oxygen reduction at $U = 0.4 \text{ V}$ for different pulsed current densities is shown in dependence on the pulse duration and pulse interval duration. Within the parameter field investigated, the maximum current density of 290 mA/mg is obtained at a pulsed current density of 1000 mA/cm², a pulse duration of 2 ms and a pulse interval duration of 10 ms (see Fig.4). These pulsing parameters are identical with the parameter combination No.8 and thus in accordance with the results presented in Fig.3. As seen from Fig.4, high $t_{\text{on}}$- and $t_{\text{off}}$-values are unfavorable at high pulsed current density. For example, by increasing $t_{\text{off}}$ from 10 ms to 500 ms, the current density drops from 290 mA/mg to a value of about 30 mA/mg. With decreasing pulsed current density, the picture changes: high $t_{\text{on}}$- and $t_{\text{off}}$-values are more and more favorable. At a pulsed current density of 100 mA/cm², the maximum current density of 240 mA/mg is obtained with $t_{\text{on}} = 200 \text{ ms and } t_{\text{off}} = 500 \text{ ms}$ (see Fig.6). It is interesting to note, that the maximum...
performance obtained at medium pulsed current density of 550 mA/cm² is lower than the maxima obtained at higher and lower pulsed current density (see Fig. 5).

Generally, the influence of the pulsing parameters on the performance of the DMFC cathode can be interpreted in terms of nucleation processes, crystal growth and mass transport limitations caused by a depletion of the platinum salt. The nucleation rate, \( v_{\text{nuc}} \), increases exponentially with the overpotential of electrochemical reduction according to the following equation [6]:

\[
v_{\text{nuc}} = k_1 \cdot \exp \left( -k_2 / \eta \right) \text{s}^{-1} \text{cm}^2
\]

where \( k_1 \) is a proportionality constant and \( k_2 \) is related to the amount of energy needed for the two-dimensional nucleation. If the pulsed current density is increased, the overpotential also increases, which induces a higher nucleation rate and thus a larger number of nuclei. During the ‘on-time’, a grain growth takes place. Therefore, the combination of a high pulsed current density and a short ‘on-time’ is expected to yield a large number of small catalyst particles with a high active surface, whereas a low pulsed current density and a long ‘on-time’ should produce a small number of large particles with a small active surface. During the ‘off-time’, mostly grain growth is observed which is caused by a recrystallization of the particles. Nevertheless, also grain refinement can occur in the ‘off-time’, if inhibiting species are blocking growth centers by adsorption [11]. If we assume a progressing grain growth during the pulsing process, low \( t_{\text{on}} \) and \( t_{\text{off}} \) values combined with a high pulsed current density should be favorable to obtain small catalyst particles, a high active surface and high performance. This consideration is confirmed by the current maximum achieved with parameter combination No.8 (see table 2 / Fig.4). However, an increasing depletion of the platinum salt in the Nafion / carbon interface during the ‘on-time’ has to be considered, which is even more critical at high pulsed current density. The resulting diffusion overpotential causes a shift of the cathode potential to more and more negative values. In worst case, the reduction current is dominated by hydrogen evolution instead of platinum deposition and it is not possible to control the platinum particle size anymore. Therefore, a high pulsed current density combined with a high ‘on-time’ is unfavorable. During the ‘off-time’, the \([\text{PtCl}_2]^2\) ions diffuse to the Nafion / carbon interface and their concentration increases. In this regard, a high ‘off-time’ may be favorable. The positive effect of an increasing ‘off-time’ at low pulsed current density and high ‘on-time’ is to be seen in Fig.6. However, in most cases, a rising ‘off-time’ is unfavorable probably due to recrystallization processes.

It is also the so-called ‘duty cycle’, which is important for the electrodeposition process. The duty cycle is a measure for the ratio of \( t_{\text{on}} \) and \( t_{\text{off}} \) and is defined as

\[
\text{duty cycle (\%)} = \frac{t_{\text{on}}}{t_{\text{on}} + t_{\text{off}}} \times 100
\]

As shown by Cheh [7] and Ibl [8], the pulse limiting current density, which is the pulse current density at which the surface concentration reaches zero at the end of the pulse, increases with decreasing ‘on-time’ and duty cycle. To avoid dendrite and powder formation, the pulsed current density should stay well below the limiting current density. Especially at high pulsed current densities, the duty cycle should not be too high. In our experiments, the duty cycle ranges from 0.4 % (Exps. No. 2/5) to 95 % (Exps. No. 6/9).
We have roughly estimated, that more than 90% of the platinum salt is reduced in most of our experiments, until the pulse limiting current density is exceeded. Only in the case of the experiments No. 6 and 9, where the duty cycle is 95%, the pulse limiting current density is already exceeded after deposition of only 20% (Exp. No 9) or 70% (Exp. No 6) of the platinum salt. Independent on the pulsing conditions, in the final period of deposition, the concentration of hexachloroplatinic acid in the Nafion phase tends to zero. Then, the pulsing current will be higher than the limiting current and hydrogen evolution will take place as additional, undesired reduction process. An exact calculation of the pulse limiting current density especially in the final period is difficult, because hydrogen evolution may induce a convective diffusion inside the Nafion phase, which is impossible to determine. An accelerated diffusion of \([\text{PtCl}_6]^{2-}\) ions to the Nafion / carbon interface will decrease the thickness of the Nernst diffusion layer and increase the limiting current. Regarding the current maxima obtained in Figs. 4-6, duty cycles in the range of 20 – 30% seem to be most favorable, whereas catalyst layers prepared with very high or low duty cycles exhibit an inferior performance. This result is in accordance with data from Choi et al. [3], which reported a duty cycle of 25% to yield the best performance.

A comparison of the performance of the best cathode prepared by pulsed electrodeposition and a conventional cathode with a commercial catalyst (E-TeK) is shown in Fig. 7. It can be seen, that the cathode catalyst layer prepared by PED yields the highest current densities, that is the pulsed catalyst shows the best performance at high overpotentials of oxygen reduction. On the other hand, the commercial catalyst gives the better performance at low overpotentials. The true reason for the different slopes of the current/potential curves is not yet clear. From first XRD measurements it turns out, that the electrodeposited platinum particles are about three times larger than the platinum particles of commercial catalysts with 40 wt% platinum and 60 wt% carbon phase (12 nm vs. 4 nm). This means, that in comparison with commercial catalyst, the performance of the catalyst layers prepared by PED could be better at low overpotentials as well, if the grain size of the platinum particles could be further reduced. At the example of unsupported platinum black catalyst we have recently demonstrated, that 70 – 100% of platinum catalyst particles prepared by electro-deposition are electro-active, whereas commercial catalyst only yields a utilization of 25% [13]. If the same prediction holds for supported catalyst, a potential improvement of the cathode performance by a factor of 3-4 can be expected.

CONCLUSIONS

We have prepared DMFC cathode catalyst layers by a new preparation method based on the electro-deposition of the catalyst [12]. This technique circumvents the use of expensive galvanic baths. Instead of this, the catalyst particles, here: platinum, are deposited inside a precursor cathode catalyst layer as part of a MEA. The precursor layer consists of a mixture of hexachloroplatinic acid, Nafion solution and carbon XC 72. The hexachloroplatinic acid is dissolved in the Nafion phase and the platinum particles are deposited onto the carbon particles in the Nafion / carbon interface. This technique allows a considerable enhancement of the utilization of the catalyst, as shown in [13]. To control the size of the platinum particles, the method of pulsed electro-deposition (PED)
was used [4,5]. The deposition was optimized by varying the pulsing parameters: pulse current density (\(j_{\text{pulse}}\)), pulse duration (\(t_{\text{on}}\)) and pulse interval duration (\(t_{\text{off}}\)). The performance of the DMFC cathodes was characterized by quasi-stationary current/potential measurements of oxygen reduction.

It turns out, that the performance of the electro-deposited catalyst layers differs by more than one order of magnitude, depending on the pulsing conditions. Within the parameter field investigated, the best cathode performance is obtained at high pulse current density and low ‘on’- and ‘off-time’ (\(j_{\text{pulse}} = 1000\) mA/cm\(^2\), \(t_{\text{on}} = 2\) ms, \(t_{\text{off}} = 10\) ms). A second maximum is obtained at low current density and high ‘on’- and ‘off-time’ (\(j_{\text{pulse}} = 100\) mA/cm\(^2\), \(t_{\text{on}} = 200\) ms, \(t_{\text{off}} = 500\) ms). These maxima are explained as the result of nucleation and grain growth effects, depletion of platinum salt nearby the reaction zone and undesired side reactions like hydrogen evolution. The ‘duty cycle’, which is proportional to the ratio of \(t_{\text{on}}\) and \(t_{\text{off}}\), is also important for the electrodeposition process. The best performance is obtained with duty cycles of 20 – 30 \%, which is in accordance with literature data [3].

Compared with commercial E-TeK platinum catalyst, the electro-deposited catalyst shows a higher current density at high overpotentials of oxygen reduction, but a lower performance at low overpotentials. In average, the performance of both catalysts is similar. We assume, that this result is due to contradicting effects, which approximately compensate each other: On the one hand, the size of the electro-deposited platinum particles (11 nm) is about three times larger compared to the size of commercial catalyst particles, which comes out from X-Ray diffraction measurements. Considering the same catalyst loading, the overall platinum surface should be lower by the same factor. On the other hand, the utilization of the electro-deposited particles is assumed to be 3-4 times higher than the platinum particles in a catalyst layer prepared by conventional technique. This assumption is based on results obtained with platinum black catalyst layers prepared by pulsed electro-deposition [13]. However, this has to be proved also for supported catalyst layers by determination of the platinum particle size (XRD and TEM measurements) as well as the active surface (cyclic voltammetry). If the assumption is true, a further optimization of the electro-deposition process regarding a reduction of the particle size should considerably improve the DMFC cathode performance.

ACKNOWLEDGEMENTS

We gratefully acknowledge the financial support of this work by the MSWWF of North-Rhine-Westfalia.
REFERENCES

Journals

1. J. McBreen, J. Electrochem. Soc. 132, 112 (1985)
2. E.J. Taylor, E.B. Anderson and N.R.K. Vilambi, J. Electrochem. Soc. 139, L45 (1992)
3. K.H. Choi, H.S. Kim and T.H. Lee, J. of Power Sources 75, 230 (1998)
4. H. Natter, T. Krajewski and R. Hempelmann, Ber. Bunsenges. Phys. Chem. 100, 55 (1996)
5. H. Natter and R. Hempelmann, J. Phys. Chem. 100, 19525 (1996)
6. B.R. Kaischew, E. Budewski and J. Malinowski, Zeitschrift für Physikalische Chemie 204, 348 (1955)
7. H.Y. Cheh, J. Electrochem. Soc. 118, 551 (1971)
8. N. Ibl, Surface Technology 10, 81 (1980)

Society Proceedings Series

9. S. Srinivasan, O.A. Velev, A. Parthasarathy, D.J. Manko and A.J. Appleby, NASA Conf. Publication 3125, April 11-13, 1989
10. A. Havránek, K. Klafki and K. Wippermann, Proc. of the Symposium 'Direct Methanol Fuel Cells', 199th ECS meeting, Eds.: S. Narayanan, S. Gottesfeld and T. Zawodzinski, The Electrochemical Society Proceedings, Pennington, NJ, 2002

Books

11. J.-C. Puippe, F. Leaman (Eds.), 'Theory and practice of pulse plating', American electroplaters and surface finishers society, Orlando, Florida / USA

Patents

12. J. Divisek, H.-F. Oetjen and V.M. Schmidt, DE No. 19720688, May 16, 1997

Diploma thesis

13. B. Ćudina, Diploma thesis, Forschungszentrum Jülich / Fachhochschule Aachen – Abteilung Jülich, July 2001
Fig. 1: Scheme of the thermostated vessel used for the electrochemical deposition of platinum in the cathode precursor layer of a DMFC MEA.

Fig. 2: Scheme of the pulsed current density vs. time.

\[ J_{\text{pulse}} / \text{mA} \cdot \text{cm}^2 \]

\[ H_2[PtCl_6] + 4H^+ + 4e^- \rightarrow Pt + 6H^+ + 6Cl^- \]
Fig. 3: Quasi-stationary current/potential curves (dU/dt = 0.5 mV/s) of oxygen reduction on Pt prepared by PED with nine different pulsing conditions (see table 1), T = 80 °C, oxygen

Fig. 4: Calculated current density of oxygen reduction in electro-deposited Pt catalyst layers as a function of the pulsing parameters ton and toff, j\textsubscript{pulse} = 1000 mA/cm\textsuperscript{2}; measuring conditions: dU/dt = 0.5 mV/s, U = 0.4 V, pure oxygen.
Fig. 5: see Fig. 4, $j_{\text{pulse}} = 550 \text{ mA/cm}^2$

Fig. 6: see Fig. 4, $j_{\text{pulse}} = 100 \text{ mA/cm}^2$
Fig. 7: Quasi-stationary current/potential curves (dU/dt = 0.5 mV/s) of oxygen reduction, comparison of DMFC cathode catalyst layers prepared by PED and with commercial E-TeK catalyst, T = 50 °C, oxygen.