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Pulse electrodeposited cathode catalyst layers for PEM fuel cells

A. Egetenmeyer^{a,c,*}, I. Radev^{b,d}, D. Durneata^c, M. Baumgärtner^a,
V. Peinecke^b, H. Natter^c, R. Hempelmann^c

^a Research Institute for Precious Metals and Metal Chemistry (fem), Katharinenstr. 17, 73525 Schwaebisch Gmünd, Germany

^b The Fuel Cell Research Center, Carl-Benz-Str. 201, 47057 Duisburg, Germany

^c Department of Physical Chemistry, Saarland University, Campus B2.2, 66123 Saarbruecken, Germany

^d Acad. Evgeni Budevski Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Sciences, Acad. G. Bonchev str., bl. 10, 1113 Sofia, Bulgaria

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ABSTRACT

Nanostructured Pt and Pt₃Co cathodes for proton exchange membrane fuel cells (PEMFCs) have been prepared by pulse electrodeposition. For high utilization the catalyst nanoparticles are directly deposited on the microporous layer (MPL) of a commercial available gas diffusion layer (GDL). In order to increase the hydrophilic nature of the substrate surface and thus improve drastically the electrodeposition process and the fuel cell performance, prior to electrodeposition, the carbon substrate is submitted to O₂/Ar plasma activation. Cathodes with different amounts and distributions of Aquivion ionomer within the cathode catalyst layer (CCL) thickness (“homogeneous”, “gradient” and “anti-gradient”), different catalysts (Pt and Pt₃Co) at varied plasma duration and catalyst loading have been prepared. The cathodes are analysed via attenuated total reflection (ATR-IR), goniometer, SEM, 0.5 M H₂SO₄ half-cell and 25 cm² H₂/Air single PEMFC. The highest single fuel cell performance is obtained for 2 min plasma activated Pt₃Co cathode.

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Introduction

Proton exchange membrane fuel cells (PEMFCs) have been receiving increasing attention as electric power source for mobile, stationary and portable applications [1–3]. Despite the advantages of PEMFCs a major barrier that needs to be overcome is the sluggish kinetics of the oxygen reduction reaction at the cathode side (ORR) [4,5]. In terms of stability and

performance platinum based materials are still the most effective catalysts used in both anode and cathode. However, the high costs and scarce resources of platinum require an increase in utilization and durability [6–8]. In common electrode preparation techniques, like rolling or spraying [9], many of the platinum atoms are not immersed in the three phase reaction zone where ionic, electronic, catalytic and gas pathways co-exists and are therefore electrochemically inactive which increases the cost but not the performance [10].

* Corresponding author. Research Institute for Precious Metals and Metal Chemistry (fem), Katharinenstr. 17, 73525 Schwaebisch Gmünd, Germany.

E-mail address: egetenmeyer@fem-online.de (A. Egetenmeyer).

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Electrodeposition is a promising, precise, scalable, rather straight forward process for deposition of uniformly distributed catalyst particles at the most effective contact zone. This ultimately allow a reduction in platinum loading at a given fuel cell performance [11].

Since the first publication in 1992 [12], platinum electrodeposition for fuel cell application has been studied by several researchers all pursuing the same aim: deposition of small particles in the three phase reaction zone [5,11,13–23]. Compared to direct current electrodeposition (DC) pulse current electrodeposition has many advantages in terms of control of nucleation density and morphology. The periodic pulsed current (usually square wave pulses) introduces continuously changing conditions at the electrode surface. Thus, the properties of the deposits can be influenced more strongly. For the electrodeposition of high surface area PEMFC catalyst materials it is important that the nucleation is favoured over the crystal growth. During pulse electrodeposition this can be achieved by lowering the surface diffusion rates of the ions, reducing the population of ad-atoms or in general by an increase of the cathode over potential during electrodeposition by applying short high current density pulses [13,24–27]. Furthermore, additional impregnation of the electro catalysed electrode with a dilute solution of the electrolyte affects the electro catalytic activity by extension of the interfacial region of the three phase reaction zone resulting in increased Pt catalysts utilization. Numerous studies have been reported on the effect of ionomer content on the cell performance [28–33]. Based on the fact that morphology, composition, loading and particle size of each gas diffusion and cathode catalyst layer (CCL) is different they indicated slightly different ionomer loadings as an optimum. However, these results show that an optimal ionomer content and distribution could enhance the fuel cell performance whereas an excessive or to low ionomer loading causes ohmic and mass transport losses particularly at high current densities [34].

A further approach for increasing the catalyst activity, thus reducing catalyst loading and costs, is to use additional materials to pure platinum [5,22]. Mayrhofer et al. [35] calculated the activity towards the ORR of several Pt-3d metal alloys. They show enhancements in the electro catalytic activity by alloying platinum with nickel and cobalt. The alloying process causes a change in the Pt–Pt bond distance and shift of the d-band centre of Pt. This leads to lower adsorption strength of oxygenated species and faster electro reduction of these intermediates [36,37].

A challenge for direct electrodeposition of platinum nanoparticles on the gas diffusion layer is the aggregation during electrodeposition because of the hydrophobic nature of the substrate and the additional microporous layer (MPL). It is known from the literature, that the exposed surface of a carbon-polymer composite material could be passivated by a layer of the polymer component that shields the conductive carbon particles [38,39]. Therefore, in order to improve the electrodeposition process by increasing the surface energy, research has been performed on pre-activation treatments of the MPL. Approaches could be adding of an additional hydrophilic layer [13] or different chemical and electrochemical treatments to promote the formation of specific chemical groups [17,18,40,41]. Martin et al. [17] treated the carbon

substrate via potential cycling prior to electrodeposition to rise the generation of oxygen functional groups.

In order to get a homogenous fine grained catalyst layer we used plasma etching for activation of the MPL surface. Plasma etching is an easy to control, reproducible, time-efficient, non-polluting and surface sensitive method. An optimization of the plasma parameters such as gas content, power, distance between the electrodes and pre-treatment (activation) time would also prevent the unnecessary deep penetration of the electrolyte solution into the GDL and electrodeposition at inactive sites inside and beyond the microporous carbon structure. Furthermore, the activation duration is much shorter compared to other methods. Plasma technique has found an application in both - research and industry but only a few papers have been published reporting the treatment of carbon materials, and thereby almost exclusively carbon nanotubes [42–44]. In the case of carbon nanotubes (CNT), plasma treatment should activate the nonreactive nature of the CNT, thus avoiding aggregation due to changing their surface chemical composition by incorporation oxygen-containing groups. Additionally, plasma treatment is used in the literature for generation of chemically reactive carbon surfaces for biomolecule immobilization [45,46]. The effect of oxygen plasma treatment on the PTFE surface is reported in the literature referring on the exact terms of the plasma source. Wilson et al. [47] found that O₂ plasma treatment results in a slight defluorination whereas other groups detected an increase in the amount of oxygen on the PTFE surface combined with defluorination.

The aim of this work is the investigation and optimization of the plasma process for CCL electrodeposition. Especially under low humidity a thin hydrophilic layer on the top of the MPL could decrease the membrane dehydration and increase the fuel cell performance [48]. A further objective of this study is the increase of the cathode catalyst utilization and overall enhancement of the fuel cell performance via: (i) optimized pulse electrodeposition procedure for platinum and platinum–cobalt catalysts; (ii) optimization of the plasma activation time; (iii) optimization of the ionomer loading and distribution within the cathode catalyst layer (CCL) and (iv) varying the cathode catalyst loading. The electrochemical tests are performed in 0.5 M H₂SO₄ half-cell and 25 cm² single PEMFC.

Experimental

Preparation of the electrodes/MEAs

The commercial carbon paper H23C8 (Freudenberg FCCT, Weinheim, Germany) is treated prior to electrodeposition using different periods of plasma etching (2, 10 and 15 min) in order to optimize the wettability and the electrodeposition process. The pressure during plasma activation is 3×10^{-2} mbar using a mixture of argon and oxygen at a gas flow rate ratio $q(\text{Ar})/q(\text{O}_2)$ of 4/3. Plasma excitation is carried out using pulsed DC with a frequency of 150 kHz and pulse duration of 1.5 μs . For deposition of platinum the plating bath contains 1 g/l Pt as Pt(NO₂)₂(NH₃)₂ (METAKEM), 70 g/l NaCH₃COO (SIGMA-ALDRICH), 100 g/l Na₂CO₃ (SIGMA-ALDRICH) and

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