

A novel non-carbon gas diffusion layer for PEM water electrolysis anodes

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The work presents a research on the development of novel gas diffusion layer (GDL) suitable for application in PEM water electrolysis. The traditionally used carbon-based GDL is replaced by GDL containing sub-stoichiometry Magneli phase titanium oxide. The newly developed GDE is integrated in a membrane electrode assembly (MEA) containing highly active Pt catalyst and proton conductive polymer electrolyte membrane. The MEA performance is characterized in a laboratory PEM electrolyser at standard operative conditions by cyclic voltammetry and steady state polarization techniques. It is found that the new layer ensures excellent electrical conductivity and has very good stability at high anodic potentials. The determined morphology factors of the platinum catalyst however, show that further optimization of the porosity is required in order to improve the water transport to the reactive zone and the catalyst utilization.

Keywords: gas diffusion layer, PEM water electrolysis, Ebonex, membrane electrode assembly

INTRODUCTION

PEM water electrolysis (PEMWE) is an innovative technology for production of hydrogen, offering several advantages overall the traditional methods such as high efficiency, low current losses, and excellent (more than 99.99%) purity of the produced gasses. The usage of polymer proton conductive membrane as an electrolyte is also very favorable since it allows the size of the electrolyzer to be dramatically reduced and avoids hazardous leakages in the environment. All these advantages make PEM water electrolysis a very attractive and highly efficiency technology. The main energy converting component in the PEMWE is the membrane electrode assembly (MEA) which consists of two gas diffusion electrodes separated by the polymer electrolyte membrane. The gas diffusion layer (GDL) is an important part of the gas diffusion electrode, providing the water flow to the reactant zone where the electrochemical reactions take place, the removal of the produced gases (H_2 and O_2), and serving as a current collector. Therefore, the performance of PEMWE strongly depends on the properties of GDL. It has to possess a low resistant micro porous structure and optimal hydrophobicity. The traditional GDLs broadly used in PEM fuel cells are based on carbon

materials - carbon blacks (mainly XC72), carbon fibers, nanotubes etc. [1]. In order to provide the required hydrophobicity, different agents such as polytetrafluoroethylene (PTFE) [2-4], polyvinylidene fluoride (PVDF) [5], fluorinated ethylene propylene (FEP) are used [6-7]. The GDL preparation includes mixing of carbon with the hydrophobic agent at optimized ratio, spreading of the obtained emulsion on an electrically conductive carrier, drying, and thermal treatment at elevated temperature to form a homogeneous porous layer. The commercially available GDLs based on carbon black XC72 provide excellent electrical conductivity and highly developed surface area but are not stable at the operative potentials of PEM water electrolysis (generally above 1.8 V). At such high anodic potentials the carbon is easily oxidized to CO_2 leading to lose of electrical conductivity, decrease of the catalyst active surface area, gradual decomposition of the anode, and degradation of the whole MEA.

The aim of this work was to develop a new gas diffusion layer, stable at the high anodic potentials typical for the oxygen evolution reaction in PEM water electrolysis. The chosen material for the replacement of carbon is a nonstoichiometric titanium oxide known under the commercial name Ebonex® (Atraverda, UK) having excellent electrical conductivity and high stability to oxidation.

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EXPERIMENTAL

Catalyst

The novel gas diffusion electrode was prepared using a commercial product Ebonex® (Atraverda, UK), which is a mixture of Magneli phase titanium oxides with common formula Ti_nO_{2n-1} . This material has unique properties among which an electrical conductivity closes to that of the metals ($\approx 1.103 \text{ S.cm}^{-1}$) and corrosion resistance approaching that of ceramics both in acid and in alkaline media [8]. A disadvantage of Ebonex in view of its application as a GDL is the large size of the particles ($5\mu\text{m}$) resulting in a low surface area ($4 \text{ m}^2.\text{g}^{-1}$). To reduce the particles size, the commercial product was treated mechanically in a planetary ball mill for 40 h. The obtained much finer powder (particle size in the range 40-60 nm) was mixed with isopropanol and stirred with a magnetic stirrer at temperature of 60°C until a homogeneous suspension was formed. After that a polytetrafluoroethylene emulsion (Teflon®, DuPont, 0.95g.ml^{-1}) was added drop wise to achieve Ebonex/PTEF ratio 70/30 wt. %. The obtained paste was spread over a carbon cloth (DeNORA), dried at 80°C for 30 min and weighted. The procedure was repeated to obtain a loading of 10 mg.cm^{-2} . The next step was sintering at 360°C for 30 minutes to create the required porous structure of the layer. To prepare a MEA for PEM water electrolysis, thus obtained GDL was loaded with 5 mg.cm^{-2} Ebonex-supported Pt catalyst forming the oxygen evolution electrode (anode) which is the working electrode under study. The cathode (hydrogen evolution electrode) was a commercial electrode with a carbon-based GDL and Pt/C catalyst (E-TEK, 40 wt. % Pt) with the same loading. Both electrodes were hot pressed on a proton conductive polymer electrolyte membrane Nafion® 117 (DuPont, USA) applying the laboratory procedure described elsewhere [9]. The evaluation of the newly developed GDL was performed by cyclic voltammetry and steady state polarization techniques in a self made laboratory cell, consisting of two gas compartments where the reactions of hydrogen and oxygen evolution take place, separated by the MEA and a reference electrode (E-TEK 40 wt. % Pt) situated in the H_2 compartment. The electrochemical tests were performed at 20°C (room temperature) and 80°C (typical operative temperature for PEMWE).

All electrochemical measurements were carried out with a commercial Galvanostat/ Potentiostat POS 2 Bank Elektronik, Germany.

RESULTS AND DISCUSSION

In the last years Ebonex has been intensively studied as an alternative catalyst support [9]. In addition to the already mentioned unique properties, namely the high electrical conductivity and corrosion resistance, this material due to its hypo-d-electron character is capable to interact with hyper-d-electron metals such as Pt, Ni, Co etc. which results in well defined synergetic catalytic effects [9, 10]. Since the commercial product has low surface area, usually a mechanical treatment is necessary in order to reduce the size of the particles. The exact parameters of this treatment (gaseous atmosphere, temperature, duration, etc.) have been optimized to achieve a reliable process leading to essential decrease in the size of the particles and a tenfold increase in the surface area, measured by BET method (from 4 to $40 \text{ m}^2.\text{g}^{-1}$). These effects, highly desirable when Ebonex is used as catalytic support, are also required for its application as a replacement of the commonly used carbon materials in GDLs.

Fig.1 and fig. 2 present the XRD spectra and the SEM images of the as-obtained and the mechanically treated Ebonex, respectively. The results show that the crystallinity of the material after 40 hours of mechanical activation sustains, while the size of the particles is visibly reduced.

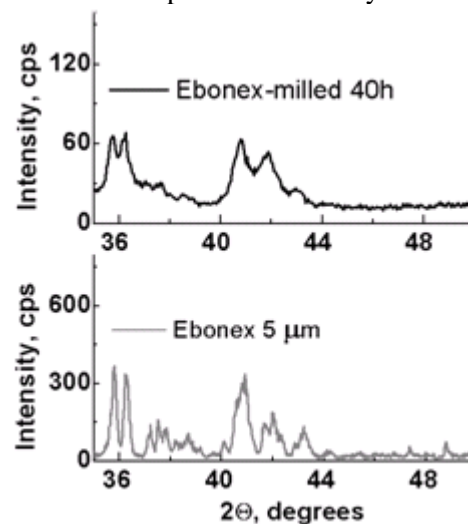


Fig. 1. XRD spectra of Ebonex before and after 40 hours mechanical treatment

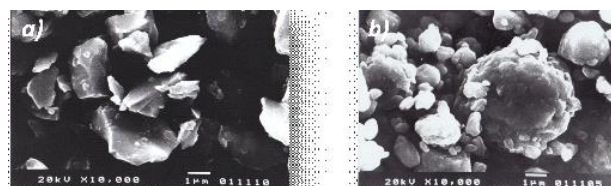


Fig. 2. SEM images of Ebonex a). before and b). after 40 hours mechanical treatment

The Ebonex-based gas diffusion layer was prepared using the mechanically treated material mixed with PTFE in accordance with the already described procedure. A membrane electrode assembly with an anode (as working electrode), containing this novel GDL and a cathode (a counter electrode) with a standard carbon-based GDL, both having catalytic loading of 0.5 mgPt.cm^{-2} was tested in the laboratory PEM electrolysis cell presented schematically in fig. 3.

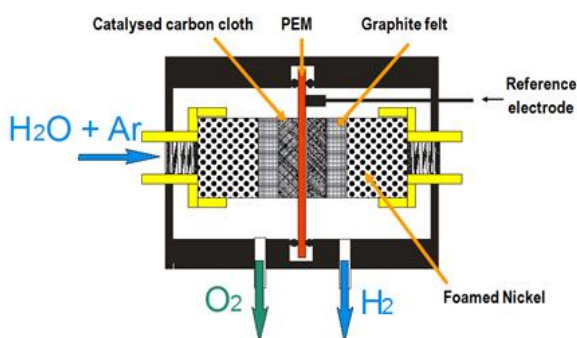


Fig. 3. Principle scheme of the laboratory PEM water electrolyser

Fig. 4 presents the cyclic voltammetry curves recorded in the potential range of water electrolysis (-0.1 to 1.8V) after different numbers of potential cycles. All current peaks typical for Pt are well depicted at the corresponding potentials in the hydrogen and oxygen ranges. The shape of the curve is characteristic for an electrode with comparatively low porosity and a crystalline Pt catalyst with a prevailing (111) orientation. The latter has been proven previously by XRD and SEM analysis [11], while the former can be explained by the high density and comparatively low specific surface area of Ebonex (3600 kg.cm^{-3} and $1\text{-}3 \text{ m}^2.\text{g}^{-1}$ compared to 264 kg.cm^{-3} and $254 \text{ m}^2.\text{g}^{-1}$ for carbon black XC72) [8]. The area under the CV curve and its shape do not change with the potential cycling (the curves of the 10th and 100th cycles are identical). At the same time, the anodic current peak at about 0.7-0.8V related to oxidation of carbon, that is characteristic for electrodes with carbon-based GDLs, is not seen on the CV.

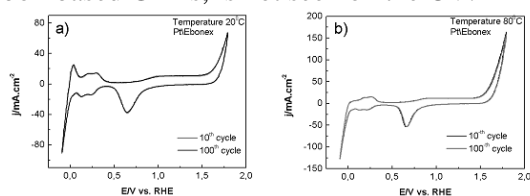


Fig. 4. CV curves of Pt/Ebonex anode with Ebonex-based GDL after different number of potential cycles in the range -0,1 to 1,8V, scan rate 100 mV.s^{-1} and working temperature a) 20°C and b) 80°C

The experimental data demonstrate stable performance of the anode under study at the applied aggressive operative conditions – oxygen in presence of moisture and high temperature.

To investigate the electrode stability at close to real operative conditions and to verify the protective properties of the new GDL (expected and demonstrated by the cyclic voltammetry results), potentiostatic tests at high anodic potentials of intensive oxygen evolution were performed. In fig. 5 are compared the anodic polarisation curves obtained at 1,8 V at room and elevated temperatures. The current reaches quickly a stable value and does not change further during the test duration. The electrode performance at 80°C is superior due to the lower activation energy of the process. The inset graph presents the performance of the electrode for a period of 24 hours at this typical PEMWE temperature. No changes in the curve and degradation phenomena both of the catalyst and GDL are registered, confirming the stability of thus prepared MEA. On the other hand, the obtained values of the current density are lower in comparison to those obtained previously for the same catalyst deposited on a carbon-supported GDL [9].

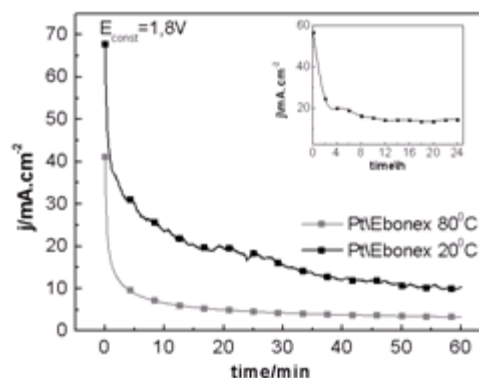


Fig. 5. Potentiostatic polarization curves of the electrode under study at different temperatures and test duration

In order to estimate the real active surface available for the electrochemical reaction of interest, the morphological factor (f) serving as a measure for the unusable part of the catalyst was calculated. The approach firstly suggested by da Silva [12, 13] is based on a repetitive potential cycling in the water window potential range (-0.1 to 1,8 V) at varying scan rate ($5 - 300 \text{ mV.s}^{-1}$) followed by determination of the anodic current density (j_a) at fixed potential, just before the beginning of intensive oxygen evolution. The morphology factor is determined from the dependence of the current density on the scan rate (v). The slope of the linear section of the curve at

low scan rates is a measure for the capacity of the total active electrode surface (C_t), while the slope at high cycling rates represents the easily accessible electrode surface (C_{ext}). The difference between both values gives the capacity of “internal”, hardly accessible part of the catalytic film (C_{int}) and the ratio C_{int}/C_t determines the morphology factor f .

The obtained experimental data of j_a (at potential of 1,6V) as function of scan rate are illustrated in fig. 6. There are two well distinguished linear regions of the curve, suggesting that at high scan rates part of the electrode surface is not accessible for the reaction. The calculated value of the morphology factor is about 0,7. This means that only about 30% of the Pt in the catalytic layer is used efficiently. For comparison, the typical catalyst utilization in MEA with a carbon-based GDL is more than 60% [14].

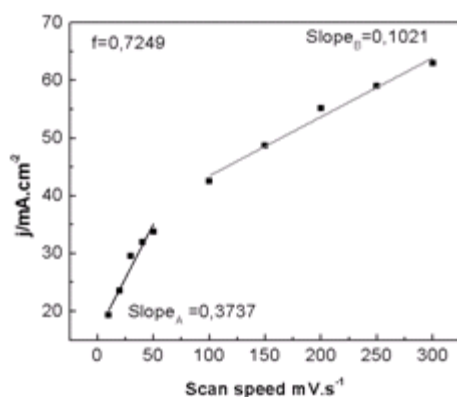


Fig. 6. Dependence of current density j_a at 1.6 V on the scan rate v

The results obtained prove the stability of the developed Ebonex-based GDL to oxidation at the conditions of PEM water electrolysis. The low current density and the calculated values of the morphology factor however, support the CV data implying insufficient porosity. To improve further the properties of this novel GDL, it is necessary to optimize the process of sintering during which the porous structure is formed.

CONCLUSION

A new GDL based on Ebonex, suitable for application in PEMWE was developed. The research performed proved a stable electrochemical behavior at high anodic potentials. The new gas diffusion layer prevents degradation of the anode, ensuring a reliable work of MEA and long term

service of the electrolyser. The obtained results established insufficient porosity of the electrode which requires further optimisation of GDL preparation procedure in order to improve the utilization of catalyst and thus, the efficiency and cost of electrolysis.

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НОВ НЕСЪДЪРЖАЩ ВЪГЛЕРОД ГАЗОДИФУЗИОНЕН СЛОЙ ЗА АНОДИ В ПЕМ ВОДНА ЕЛЕКТРОЛИЗА

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(Резюме)

Настоящата работа е базирана на разработването на иновативен газодифузионен слой, приложим във водните електролизьори с полимерна протонпроводяща мембрана. Традиционно използваните въглеродни газодифузионни слоеве са заменени със слоеве, базирани на нестехеометричен титаниев оксид Magneli фаза. Новият газодифузионен слой (ГДС) е интегриран в мембранен електроден пакет (МЕР), който съдържа високо активен платинов катализатор и полимерна протонпроводяща мембрана. МЕР е охарактеризиран лабораторно в ПЕМ електролизна клетка посредством методите на цикличната волтаметрия и различни поляризационни техники. Установено е, че новият ГДС има добра електрическа проводимост и стабилно поведение при високи анодни потенциали. Стойността за морфологичния фактор на платиновия катализатор обаче показва, че е необходима по-нататъшна оптимизация на структурата на ГДС, с цел увеличаване на порьозността му и съответно подобряването на доставката на реагент до катализатора и неговото по-пълно оползотворяване.