Short communication

Towards developing a backing layer for proton exchange membrane electrolyzers

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HIGHLIGHTS

- A thermally sprayed titanium MPL for PEM electrolyzers has been developed.
- SEM images revealed a micro-size pore structure and high rugosity.
- The MPL reduces contact resistance by ca. 20 mΩ cm^2.
- The improvement in the PEM electrolyzer has been confirmed by EIS.
- The MPL enhances significantly the performance at high current densities.

GRAPHICAL ABSTRACT
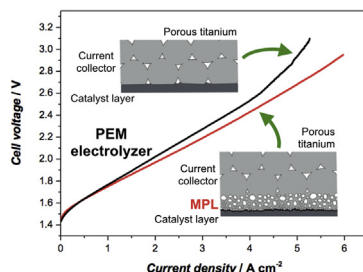
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ABSTRACT

Current energy policies require the urgent replacement of fossil energy carriers by carbon neutral ones, such as hydrogen. The backing or *micro*-porous layer plays an important role in the performance of hydrogen proton exchange membrane (PEM) fuel cells, reducing contact resistance and improving reactant/product management. Such carbon-based coating cannot be used in PEM electrolysis since it oxidizes to CO_2 at high voltages. A functional titanium *macro*-porous layer (MPL) on the current collectors of a PEM electrolyzer is developed by thermal spraying. It improves the contact with the catalyst layers by ca. 20 mΩ cm^2, increasing significantly the efficiency of the device when operating at high current densities.

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1. Introduction

Hydrogen can be used as a carbon neutral energy carrier either to provide electricity through fuel cells or to store the surplus coming from renewable sources such as solar or wind by means of water electrolysis systems [1]. Proton exchange membrane (PEM) electrolyzers have great technological potential thanks to the high power densities, superior gas quality and superior dynamic operation ranges [2]. Up to now, the current collector (CC) of a PEM electrolyzer consists of a porous structure of titanium such as a sintered disc, foam, felt or expanded mesh [3]. The porosity and pore size of the sintered discs can be adjusted by selecting the appropriate size and shape of the titanium particles [4] but the configurations are quite limited. Foams, felts and expanded meshes overcome these issues [5] and have a lower cost [6]. However, the

Abbreviations

CC	current collector
CL	catalyst layer
CPE	constant phase element
EIS	electrochemical impedance spectroscopy
GDL	gas diffusion layer
ICR	interfacial contact resistance
LR	leakage rate
MPL	macro-porous layer
OER	oxygen evolution reaction
PEM	proton exchange membrane
PMG	precious metal group
PTFE	polytetrafluoroethylene
SEM	scanning electron microscopy
VPS	vacuum plasma spraying

development of a CC with optimized microstructure for efficient water/gas bubble management is still a challenge in PEM electrolysis. F. Arbabi et al. used a technique of visualization of air injection into the liquid-saturated porous network of microfluidic chips in order to simulate the transport mechanism of gas bubbles in the CC [7,8]. They found that transport mechanism of air bubbles in the CC is capillary-dominated even at high current densities. Their results showed that gas saturation at the breakthrough moment is smaller for felts than for the sintered discs.

The uniform and sufficient contact between the CC and the catalyst layer (CL) reduces the interfacial contact resistance (ICR) and thus the activation overpotential [9]. The ICR can be lowered by using expensive precious metal group (PMG) coatings on the CC [10]. In the case of a PEM fuel cell this problem is solved by introducing a backing or micro-porous layer between the catalytic layer and the carbon CC or gas diffusion layer (GDL) [11,12]. It lowers the ohmic losses by keeping the membrane better hydrated improving the adhesion and contact between the various conductive components, such as carbon [11]. In addition, it allows for better transport of the various species required for reaction by removing the produced H_2O through its hydrophobic component. Lastly, the backing layer in a PEM fuel cell buffers regions between the diffusion media and the CL [12]. C. M. Hwang produced a backing layer for PEM unitized reversible fuel cells by loading Ti felts with Ti powder and polytetrafluoroethylene (PTFE). The modification of the GDL showed a marked improvement when the electrochemical device operated in fuel mode, but had not effect when operating as electrolyzer [5]. Other attempts have been carried out to produce a backing layer for PEM electrolyzers with coatings of Ir and Ti powder [13,14]. Yet, all the benefits that the backing layer offers to the PEM fuel cell, reported in more than 149 publications since 2002 (ISI Web of Knowledge), are hitherto missing in a PEM electrolyzer. Herein we provide an approach for developing a titanium macro-porous layer (MPL) produced by vacuum plasma spraying (VPS) on the CC of a PEM electrolyzer.

2. Experimental

Porous titanium coatings were deposited by vacuum plasma spraying (VPS) on 5×5 cm^2 sintered titanium filters (SIKA-T 10, GKN Sinter Metals). The morphological characteristics of the sintered titanium CC are summarized in Table 1. Only the side of the CC that is in contact with the CL is coated. Grade 1 titanium (grain size < 45 μm, TLS Technik Spezialpulver) was used as feedstock

Table 1
Morphological characteristics of the sintered titanium CC.

Property	Approximate values
Thickness of the CC	1000 μm
Porosity	40%
Particle shape	Irregular
Particle size	100–200 μm
Minimum pore size	>1 μm
Maximum pore size	30 μm
Modal pore size	17 μm

powder. The chamber pressure of the VPS facility was 50 mbar in order to prevent the presence of O_2, which would oxidize titanium into TiO_2 at the high temperatures of the plasma. The substrates were pre-heated up to 250 °C during deposition. Gas flow rates of Ar, N_2 and H_2 were carefully chosen to achieve the highest plasma enthalpy possible (21.27 MJ kg^{-1}). The torch sweep rate was 500 mm s^{-1}. Measurements of the leakage rate (LR) parameter and ICR under compaction force were used as rough indicators of the density and electrical properties, respectively. Experimental details are reported elsewhere [15]. Cross-section images of a coated CC were taken with a SEM Zeiss ULTRA plus (secondary electron detection) with charge compensation. The accelerating voltage and working distance were 15 kV and 8.4 mm, respectively.

Electrochemical tests were performed in 25 cm^2 single PEM electrolyzer cells using the porous titanium discs as CC with and without MPL. Commercial MEAs (Greenerity® SolviCore GmbH) for water PEM electrolysis with a N115 membrane, an Ir-based anode and a Pt-based cathode, were used. Electrochemical impedance spectroscopy (EIS) measurements were realized by means of an impedance equipment (Zahner elektrik IM6) and booster (Module PP240) at different current densities in a frequency range of 1×10^5 to 2×10^{-3} Hz. The water was supplied only to the anode side of by means of a peristaltic pump at a flow rate of 1 ml s^{-1}. A deionized water resin (630 Laurent, Grandby, QC J2G 8V1, Aldex Chemical Co. LTD) was used to maintain a resistivity below 10 MΩ cm. The measurements were recorded at a scan rate of 4 mA cm^{-2} s^{-1}, 85 °C and atmospheric pressure.

3. Results

The proof of concept of a MPL with controlled porosity is illustrated in a scheme presented in Fig. 1a. As shown, the MPL should increase the contact surface with the catalyst while improving the water/gas management through a gradient of pore sizes. For this purpose, several layers of titanium were deposited on the CC. The LR was determined. It was found that two layers of titanium produced a LR of 480 mbar l cm^{-2} s^{-1}. Two more layers decreased this value down to 112 mbar l cm^{-2} s^{-1}. Further increase in the number of layers resulted in lower LR, thus higher density of the coating. Fig. 1b shows a cross section SEM image of 8-layers of porous titanium deposited on the surface of the CC by VPS. As it can be observed the layer has a splat structure, is porous, and rough. An estimation of the thickness, rugosity, pore size and porosity was carried out by image analysis. These results along with the LR measurements are summarized in Table 2. One can notice that the increase of the number of layers has practically no effect in the rugosity, which in average is about 0.74. However, it is possible to make the coating rougher by increasing the torch sweep rate. By depositing layers of titanium on mild steel and corroding the substrate afterwards it is possible to determine more accurately the pore size of a freestanding MPL by Hg-adsorption technique. It turned to be between 0.1 μm and 10 μm with a modal pore size of 1.3 μm (Fig. S1, Supporting information). The pore structure of the