



ELSEVIER

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

journal homepage: [www.elsevier.com/locate/he](http://www.elsevier.com/locate/he)

## Highly active screen-printed Ir–Ti<sub>4</sub>O<sub>7</sub> anodes for proton exchange membrane electrolyzers

Tiago Lagarteira <sup>a,b</sup>, Feng Han <sup>a,\*\*</sup>, Tobias Morawietz <sup>c</sup>, Renate Hiesgen <sup>c</sup>, Daniel Garcia Sanchez <sup>a</sup>, Adélio Mendes <sup>b</sup>, Aldo Gago <sup>a,\*\*\*</sup>, Rémi Costa <sup>a,\*</sup>

<sup>a</sup> Institute of Engineering Thermodynamics, German Aerospace Center, Pfaffenwaldring 38-40, Stuttgart, Germany

<sup>b</sup> Laboratory for Process Engineering, Environmental, Biotechnology and Energy (LEPABE), Faculty of Engineering of University of Porto, Rua Roberto Frias s/n, 4200-465 Porto, Portugal

<sup>c</sup> University of Applied Sciences Esslingen, Dep. of Basic Science, Kanalstrasse 33, Esslingen, Germany

### ARTICLE INFO

#### Article history:

Received 16 August 2017

Received in revised form

19 February 2018

Accepted 27 February 2018

Available online xxx

#### Keywords:

Proton exchange membrane water electrolysis

Membrane electrodes assembly

Catalyst coated membrane

Iridium loading

Ceramic support

Screen printing

### ABSTRACT

Electroceramic support materials can help reducing the noble-metal loading of iridium in the membrane electrodes assembly (MEA) of proton exchange membrane (PEM) electrolyzers. Highly active anodes containing Ir-black catalyst and submicronic Ti<sub>4</sub>O<sub>7</sub> are manufactured through screen printing technique. Several vehicle solvents, including ethane-1,2-diol; propane-1,2-diol and cyclohexanol are investigated. Suitable functional anodic layer with iridium loading as low as 0.4 mg cm<sup>-2</sup> is obtained. Surface properties of the deposited layers are investigated by atomic force microscopy (AFM). The most homogeneous coating with the highest electronic conductivity is obtained using cyclohexanol. Tests in PEM electrolyzer operating at 1.7 V and 40 °C demonstrate that the CCM with anode coated with cyclohexanol presents a 1.5-fold higher Ir-mass activity than that of the commercial CCM.

© 2018 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

### Introduction

Intermittency and fluctuation of renewable energy sources remain major issues for an efficient utilization, while the power flow and utility frequency of the grid need to be steadily regulated and balanced. Hydrogen can be produced through water electrolysis with the surplus from renewables when available and stored as a carbon neutral energy carrier. Proton

exchange membrane (PEM) water electrolysis is a promising technology for coupling renewables with hydrogen due to the wide operating range and the fast response [1–3]. In particular, the compact system design, high efficiency and easy maintenance are advantageous features comparing to the mature alkaline electrolysis technology [1,4,5]. Yet, the penetration of PEM electrolyzer systems at the megawatt scale will be hindered by the high cost and scarcity of catalyst materials, together with the manufacturing of the membrane electrodes

\* Corresponding author.

\*\* Corresponding author.

\*\*\* Corresponding author.

E-mail addresses: [feng.han@dlr.de](mailto:feng.han@dlr.de) (F. Han), [aldo.gago@dlr.de](mailto:aldo.gago@dlr.de) (A. Gago), [remi.costa@dlr.de](mailto:remi.costa@dlr.de) (R. Costa).

<https://doi.org/10.1016/j.ijhydene.2018.02.179>

0360-3199/© 2018 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

assembly (MEA), which currently represent approximately 20% of the overall costs of the PEM electrolyzer stack [6]. Therefore, there is a potential for cost reduction by decreasing the used amount of precious group metals (PGM) and optimizing the catalyst coating process in the production of MEAs.

A reduction in the catalyst loadings is not only important due to high price of the precious metals but also the scarcity of platinum and mainly iridium [7]. Despite some recent advances that took several years of research [8,9], the state-of-the-art anode still demands high iridium loadings of ca. 2–4 mg cm<sup>-2</sup> [10,11], to balance the sluggish kinetics and the high charge transfer overpotential caused by the oxygen evolution reaction (OER). Ceramic supports like Magnéli-phase titanium sub-oxides (TiO<sub>2</sub>, Ti<sub>4</sub>O<sub>7</sub> and Ti<sub>5</sub>O<sub>9</sub>) are promising catalyst supports, providing a higher catalytic stability and resistance to corrosion in the harsh environment of the electrolyzer anode in comparison to the typical carbon-based supports used in PEM fuel cells [12–20].

For the manufacturing, screen printing is a widespread and common cost-efficient printing technique that can be used to produce catalyst coated membranes (CCM-MEA), where the catalysts are directly deposited on a proton exchange membrane – typically Nafion. Some reports on the fabrication of MEAs for PEM fuel cells with screen printing are available. But in most of them, the catalyst deposition is carried out on the gas diffusion layer (GDL) or on PTFE sheets with posterior decal transfer to the membrane. This is the usual strategy to avoid typical processing issues like membrane swelling when it contacts with organic solvents [21–24]. The overcome of the swelling issue is a key challenge as direct catalyst deposition on the membrane may provide better contact between the catalyst layer and the electrolyte thus reducing interfacial contact resistances. Kim and co-workers proposed a treatment [25] in which the membrane was exchanged from the H<sup>+</sup> form to Na<sup>+</sup> form before coating. The protonic reconversion was performed after the catalyst layer was deposited and dried. Nonetheless, no report is found in the literature of screen-printed catalyst layers directly on the membrane for PEM electrolyzers [11].

Composition of the catalyst ink affects not only the coating process itself - by governing the rheological properties - but also affects the microstructure of the coated layer. The properties of the catalyst ink should be optimized not only for the coating process but also for maximizing the connection of catalytic sites to both electronic and ionic conductive phases, thus ensuring the overall performance of the electrolyzer. The idea of using solubilized Nafion ionomer in catalyst inks or suspensions has been widely accepted for extending protonic vehicular conduction inside 3D-structures of the catalyst layers [26–28]. More recently, Chan and Eikerling reported that ionomer-free ultra-thin catalyst layers (20–500 nm thick) rely

entirely on liquid water for proton conduction [29]. Therefore, a fully humidified catalyst layer would be beneficial, enabling proton conduction exclusively by the Grotthuss mechanism [30]. In the case of screen-printed catalyst layers, with thickness in the micrometer range, ionomer distribution and its orientation should be tuned for connecting the most active sites to the protonic conductive phase while not hindering electronic conductivity of the catalyst support and mass diffusion in the porous structure of the catalyst layer [31].

In this work, highly-active anodes with inexpensive catalyst support and low catalyst loading were fabricated via a cost-effective and scalable screen printing technique. Moreover, the properties of the developed layers were characterized and investigated through diagnostic tools such as TGA, AFM and electrochemical single cell tests.

## Experimental

### CCM fabrication

#### Screen printing of the anode

In the preparation of the screen printing inks, summarized in Table 1, 30 wt% Iridium Black (Umicore) was mixed with 70 wt% Ti<sub>4</sub>O<sub>7</sub> catalyst support (Changsha Purong Chemical Engineering Inc.) using a mortar and a pestle. Ethane-1,2-diol (Sigma Aldrich), propane-1,2-diol (VWR) and cyclohexanol (VWR) were used as organic solvents for the inks (physicochemical properties shown in Table 2). The ratio between Nafion ionomer and the total solid particles was kept at 30 wt% [32]. The solvents from a 20 wt% Nafion solution (Sigma Aldrich) were evaporated during the mixing and, only then, the chosen organic solvent was added. The solid content in the screen printing inks was kept at 37.5 wt%, except for the ink used in the effectiveness assessment of the membrane swelling treatment which contained a lower (but not determined) weight ratio of solid particles.

Nafion 212 membrane was cut into squares with a size 7 cm × 7 cm and, after removing the protection foils and conditioning at ambient humidity, they were weighted. Subsequently, they were placed on a porous metal substrate, enabling the use of a vacuum positioning and fixing system during the coating process. An Aurel 900 screen printer equipped with a Koenen Typ-10 M6 mesh (4 cm<sup>2</sup> of open area) was used for coating the anodes of the CCMs. The printing pressure was set to 1.5 N cm<sup>-2</sup> and the distance between the screen and the substrate was 0.8 mm.

After coating, the samples were dried firstly on the screen printing holder for 10 min under infrared radiation produced by an incandescent lamp (40 W, distance 10 cm) to remove most of the solvent, and then dried at 348 K for 30 min in a

**Table 1 – Screen printing ink formulations; weight ratios based on the total weight of the ink.**

Ink formulations	Catalyst (7.875 wt%)	Catalyst support (18.375 wt%)	Binder (11.25 wt%)	Solvent (62.5 wt%)
A	Ir black	Ti <sub>4</sub> O <sub>7</sub>	Nafion ionomer	Ethane-1,2-diol
B	Ir black	Ti <sub>4</sub> O <sub>7</sub>	Nafion ionomer	Propane-1,2-diol
C	Ir black	Ti <sub>4</sub> O <sub>7</sub>	Nafion ionomer	Cyclohexanol

Download English Version:

<https://daneshyari.com/en/article/8948298>

Download Persian Version:

<https://daneshyari.com/article/8948298>

[Daneshyari.com](https://daneshyari.com)