



Improved durability of proton exchange membrane fuel cells by introducing Sn (IV) oxide into electrodes using an ion exchange method



M.G. Poulsen ^a, M.J. Larsen ^b, S.M. Andersen ^{a,*}

^a Dep. of Chemical Eng., Biotech. & Environmental Tech., University of Southern Denmark, Campusvej 55, 5230 Odense M, Denmark

^b EWII Fuel Cells A/S, Emil Neckelmans Vej 15 A&B, 5220 Odense SØ, Denmark

HIGHLIGHTS

- Optimized ion exchange methods to introduce SnO₂ into electrodes.
- Choice of solvent influenced Sn uptake and distribution within the electrode.
- Electrodes containing SnO₂ lost less Pt when exposed to an accelerated stress test.
- SnO₂ remained stable throughout test.
- The MEA with the SnO₂-containing anode showed remarkably reduced H₂ crossover.

ARTICLE INFO

Article history:

Received 3 October 2016

Received in revised form

10 December 2016

Accepted 9 January 2017

Keywords:

Tin (IV) oxide

Ion exchange

Electrocatalyst

Durability

ABSTRACT

Electrodes of Proton Exchange Membrane Fuel Cells (PEMFCs), consisting of catalyst-coated gas diffusion layers, were subjected to an optimized ion exchange procedure, in which tin (IV) oxide (SnO₂) nanoparticles were introduced into them. Both methanol and sulfuric acid were tested as ion exchange solvents. SnO₂ has previously been shown to exhibit radical scavenging abilities towards radicals inside the electrocatalyst layers. Its presence inside the electrodes was confirmed using X-ray photoelectron spectroscopy and X-ray fluorescence. After exposure to an accelerated stress test in a three-electrode setup, the electrodes containing SnO₂ were found to have retained approximately 73.0% of their original Pt, while only 53.2% was retained in electrodes treated identically, but without Sn. Similarly, the SnO₂-treated electrodes also experienced a smaller loss in electrochemical surface area in comparison to before the accelerated stress test. A membrane electrode assembly (MEA) constructed with a SnO₂-containing anode was evaluated over 500 h. The results showed remarkably reduced OCV decay rate and end of test hydrogen crossover compared to the control MEA, indicating that SnO₂ aids in impeding membrane thinning and pinhole formation. The results point toward a positive effect of SnO₂ on fuel cell durability, by reducing the degradation of the membrane as well as of the ionomer in the electrocatalyst layer.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The proton exchange membrane fuel cell (PEMFC) is a green energy conversion technology that has been the subject of vast amounts of research during recent times [1]. Efforts have been made to make them competitive with current energy conversion technologies due to several beneficial factors such as the high

efficiency of their electrochemical processes, their clean operation, and short start-up period. The combination of these factors means that PEMFCs can be utilized as a source of renewable energy for both portable and stationary applications [2,3]. Currently, much of this research is focused on improvement of the durability and reduction of the high production costs that keep PEMFCs from full scale commercialization [4].

The membrane electrode assembly (MEA) is a complex construction which consists of several materials that show heterogeneous aging during fuel cell operation [5]. MEA degradation is

* Corresponding author.

E-mail address: mashu@kbn.sdu.dk (S.M. Andersen).

governed by a multitude of processes that ultimately lead to operational failure of the fuel cell. In the electrocatalyst layer, the platinum group metal (PGM) supported on high surface area carbon, PtX/C (where X is one of a range of other transition metals usually added), is subject to processes such as carbon corrosion [6], PtX crystallite migration [7] and PtX dissolution and redeposition [7,8]. Furthermore, the electrocatalyst layer generally contains a suitable amount of Nafion[®] or other ionomer to create a three-phase-boundary (TPB). Nafion often also constitutes the proton exchange membrane (PEM), and it is degraded through processes such as the formation of pinholes, desulfonation, and attacks from peroxide radicals [4]. This radical-induced degradation can also affect the Nafion ionomer present in the electrocatalyst layer, which is detrimental to the TPB and consequently to the utilization of the PGM catalyst. Species such as hydrogen peroxide (H₂O₂), hydroxyl radical (\cdot OH), and hydroperoxyl radical (\cdot OOH) play an important role in this process [9,10]. However, whether the majority of radicals are formed at the anode or at the cathode is debated – and it furthermore depends on operation conditions – at the cathode, hydrogen peroxide and intermediate radicals may be formed by the two-electron reduction of oxygen, while at the anode [11], the same species may form by different pathways due to oxygen crossover [12]. Vast efforts have been devoted to enhance polymer electrolyte membranes by introducing radical scavengers [13–15] through casting or impregnation to form composite membranes. Recently, Zaton et al. [16] has shown improved cell durability by incorporating cerium oxide enriched nanofibers (NFCeOx) between the membrane and the electrodes of MEAs, where the NFCeO_x acts as a shell that protects the membrane electrolyte from harmful radicals. Since the hydroxyl radical – as the initiator of a series of oxidative reactions – is formed on electrocatalysts [17], a more efficient strategy to reduce the damage is to capture the radicals on the spot. Therefore, our approach is to introduce radical scavengers in the catalyst layer in order to trap the radicals at their earliest stage, by capturing the oxidants in the vicinity of the electrocatalyst before they migrate to the membrane electrolyte.

Regarding choice of radical scavenger, cerium (IV) oxide (CeO₂) is the most studied and documented antioxidant. CeO₂ nanoparticles show scavenging abilities towards H₂O₂ and hydroxyl radicals through an oxidation-reduction cycle that continually converts CeO₂ between oxidation states Ce³⁺ and Ce⁴⁺ [18–20]. Similar to those of CeO₂, we have previously reported that tin (IV) oxide (SnO₂) also exhibits radical scavenging abilities [21]. SnO₂ is mostly known as catalyst support due to its high stability under the acidic conditions of the PEMFC and good tolerance towards CO [22,23]. Ostrovsky et al. [24] manufactured a Pt on antimony doped tin oxide (Pt/ATO) electrocatalyst using a photochemical technique that showed a significantly enhanced electrochemical stability in comparison to Pt/C, while retaining an ORR mass activity similar to that of Pt/C. Senoo et al. [25,26] synthesized Nb-doped and Ta-doped SnO₂ catalyst support materials that, when platinized and employed as cathode electrocatalysts in MEAs, exhibited higher current densities and remarkable stability in comparison to Pt on CB (carbon black) catalysts. Chino et al. [27,28] similarly worked on Nb-doped SnO₂ catalyst support materials, and related the superior performance of these materials to the hydrophilicity of the SnO₂ support and the electrical conductivity of the doped structure. Moreover, Pt/Sn composites also exhibit excellent performance as catalysts for the methanol and ethanol oxidation reactions (MOR and EOR) [29].

In this work, SnO₂ serving as a radical scavenger in the electrode layer is further explored. An optimized method was developed for the direct formation of SnO₂ *in-situ* in a catalyst-coated gas diffusion layer, based on the ion exchange method developed earlier in

our group [30]. Sn²⁺ ions were carefully ion exchanged onto the sulfonic acid groups of Nafion ionomer present in electrodes. Subsequently, they were heated to form SnO₂. Ion exchange concentration was optimized, and two different Sn ion solvents were employed (either methanol (CH₃OH) or sulfuric acid (H₂SO₄)) during the synthesis. A strong focus was placed on assuring that as little physical damage as possible was subjected to the electrodes during the procedure.

Single-cell testing was performed for MEAs containing SnO₂-anodes prepared by the above method. Indeed, poor hydration of the membrane is more likely to be an issue at the anode [31]. Studies by S. Hara et al. showed that hydrated SnO₂ possesses a high proton conductivity which is strongly dependent on the hydration level [32,33]. This proton conductivity, in addition to the hydrophilicity and radical scavenging abilities of SnO₂, is anticipated to be beneficial towards cell durability.

Aqueous solutions may be employed to facilitate the ion exchange procedure. However, swelling properties of Nafion are well known to vary greatly depending on counter ion and solvent [34,35]. In H⁺-Nafion membranes, both water and methanol have been studied extensively and show great differences in how they affect swelling [36,37]. Increased swelling of Nafion by methanol can be ascribed to methanol interacting with the hydrophobic segments of Nafion, whereas water mainly gathers in the hydrophilic clusters formed by the sulfonic acid groups [38]. Additionally, swelling properties might also be heavily influenced by the presence of inorganic salts. In the experiments by A. Randová et al. [39] it was found that Nafion swelling was reduced by the addition of such salts, and that this reduction increased with growing ionic radius of the cation.

2. Experimental methods

2.1. Chemicals

Tin (II) chloride dihydrate (SnCl₂·2H₂O) ≥99.99%, tin (II) sulfate (SnSO₄) ≥95% and methanol (CHROMASOLV[®]) ≥99.9% were acquired from Sigma Aldrich. 95–97% sulfuric acid was acquired from Merck and diluted using ultrapure water (resistivity of ≥18.2 MΩ). All chemicals were used as received.

2.2. Experimental procedure

An electrode sheet consisting of a gas diffusion layer (GDL) coated with a HISPEC[®] 9100 Pt/C catalyst (0.5 mg_{Pt} cm⁻², Nafion content of 30 wt% in the electrocatalyst layer) was initially cleaned in a bath of 1 M sulfuric acid at 50 °C for 1 h. After ended cleaning, the sheet was exposed to the same treatment in ultrapure water. Electrodes were generally prepared in sets of four. Thus, four 20 mL baths were arranged as follows: a 0.02 M solution of SnCl₂·2H₂O in methanol, a 0.02 M solution of SnSO₄ in 1 M sulfuric acid, and a bath for each of these which contained either methanol or 1 M sulfuric acid without the salts, respectively. The two latter baths would serve as controls not exposed to a Sn salt. Beforehand, each solution had been degassed with nitrogen for several minutes in order to prevent early oxidation of Sn²⁺ to Sn⁴⁺. Four electrode pieces of approximately 2 × 2 cm were cut from the electrode sheet, submerged into each their own bath, and left for 24 h for the ion exchange process to take place. The electrodes were then pulled out of their respective solutions and rinsed with ultrapure water. Immediately after, they were placed in each their bath of 20 mL ultrapure water for another 24 h to remove any remaining solvent and undissolved salts. Subsequently, they were vacuum-dried at a pressure of 0.01 mbar at 80 °C for 1 h using a VT 6025 vacuum oven (Thermo Scientific). The vacuum was then released and the

متن کامل مقاله

دریافت فوری ←

ISIArticles

مرجع مقالات تخصصی ایران

- ✓ امکان دانلود نسخه تمام متن مقالات انگلیسی
- ✓ امکان دانلود نسخه ترجمه شده مقالات
- ✓ پذیرش سفارش ترجمه تخصصی
- ✓ امکان جستجو در آرشیو جامعی از صدها موضوع و هزاران مقاله
- ✓ امکان دانلود رایگان ۲ صفحه اول هر مقاله
- ✓ امکان پرداخت اینترنتی با کلیه کارت های عضو شتاب
- ✓ دانلود فوری مقاله پس از پرداخت آنلاین
- ✓ پشتیبانی کامل خرید با بهره مندی از سیستم هوشمند رهگیری سفارشات