



Short communication

Tin Dioxide as an Effective Antioxidant for Proton Exchange Membrane Fuel Cells



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H I G H L I G H T S

- SnO₂ showed effective antioxidant ability in PEMFC electrodes.
- Different degradation segments were detected under different RH OCV treatments.
- Low humidity induces greater damage to the polymer under OCV.

A R T I C L E I N F O

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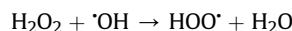
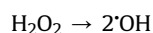
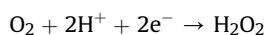
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Tin dioxide (SnO₂) containing electrodes showed significantly lower radical induced polymer degradation under single cell open circuit voltage (OCV) treatment than SnO₂ free electrodes. A backbone related segment was detected under 100% RH, and an oxygen containing side chain segment was detected under 6% RH by ¹⁹F NMR. Fluoride ion release was observed in both cases. Low humidity induces greater damage to the polymer under OCV.

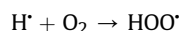
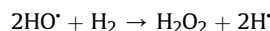
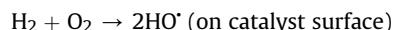
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1. Introduction

Durability is one of the most important issues impeding fuel cell technology commercialization. Radical induced perfluorinated sulfonic acid (PFSA) polymer degradation is generally considered the most important degradation mode for the polymer electrolyte in proton exchange membrane fuel cells (PEMFCs) [1,2]. Essential radicals involved in the process are the hydroxy radical ([•]OH), the hydrogen radical (H[•]) and the peroxy radical (HOO[•]) [3]. Formation of the hydroxy radical, as the initiator of a series of oxidative reactions, is formed through either decomposition of hydrogen peroxide (H₂O₂) generated via two electron oxygen reduction reaction:



or direct formation from H₂ and O₂ gasses over platinum catalyst:



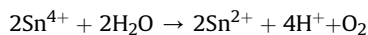
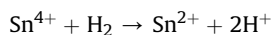
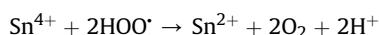
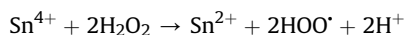
Radical induced polymer degradation mechanisms commonly considered in the literature are the back bone unzipping mechanism [4] and side chain degradations at corresponding reaction sites [5,6]. Elimination of the primary radical source is the fundamental mitigation strategy. Many species have been explored for their potential as radical scavengers, e.g. CeO₂ [7–9], MnO₂ [10], metal nanoparticles (Pt, Pd, Ag, and Au) [11] etc. However, SnO₂ has

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not been studied for any antioxidant (or radical scavenging) activity so far. Moreover, it is low-cost and bio-compatible.

In the literature, doped or un-doped SnO₂ has been applied as catalyst support in PEMFCs [12,13] and water electrolyzers [14] with promising results. The promotion of the catalyst activity and corrosion resistance was attributed to the unique catalyst–support interactions. Besides, SnO₂ supported Pt was also reported of better CO tolerance than conventional catalysts [15]. Furthermore, SnO₂ or its hydrated form had also been used as filler in protonic conductive membranes to improve mechanical properties [16,17] and to prevent methanol crossover [17].

The dual valency of Sn can facilitate a reversible transformation of the surface composition from stoichiometric surfaces with Sn⁴⁺ surface cations into a reduced surface with Sn²⁺ surface cations depending on the oxygen chemical potential of the system [18]. In analogy to CeO₂ [19], the corresponding antioxidant mechanism for SnO₂ can be schematically presented as:



In this work, SnO₂ nanoparticles were introduced in the electrode structure and tested for their antioxidant ability.

2. Experimental

Platinum and Platinum–ruthenium supported on carbon black (Hispec 9000 and 10000) were purchased from Johnson Matthey. The electrodes were fabricated following a PEMFC electrode preparation recipe, where a suspension of catalyst and Nafion[®] ionomer in water/alcohol was coated onto a gas diffusion layer (GDL) Sigracet[®] 35DC (SGL Group). SnO₂ nanoparticles were generated in-situ in the electrode polymer phase through an ion exchange procedure, described in our earlier work [16]. The exchanged

electrodes were rinsed with methanol and water repeatedly in order to eliminate any residual non-ion-exchanged SnO₂. The loading of SnO₂ was determined by the weight gain of the electrode, which corresponded to around 5–8% of the ionomer.

The final electrodes with or without SnO₂ were laminated on to a Nafion 212 membrane at 140 °C, 7 bar for 3 min, to produce membrane electrode assemblies (MEAs). In this manner, four types of MEAs were fabricated: 1) SnO₂ containing anode and original cathode labelled as **TAOC**; 2) original anode and SnO₂ containing cathode labelled as **OATC**; 3) SnO₂ containing anode and SnO₂ containing cathode labelled as **TATC** and 4) original anode and original cathode labelled as **OAOC**, which is also the control in the study. Fuel cell testing was performed with a single cell of dimension 2.5 × 2.5 cm². The cell was kept at open circuit voltage (OCV) at 100 and 6% relative humidity (RH) and 70 °C. The flows of H₂ and air applied during the OCV testing were 10 Nml min⁻¹ and 20 Nml min⁻¹ respectively. I–V performance was carried out at stoichiometry values of lambda H₂ = 2 and lambda air = 4. The system was controlled and monitored by an electrochemical workstation (IM6e, ZAHNER and a homebuilt setup based on MACCOR hardware).

All NMR experiments were performed in a Bruker 400 MHz NMR spectrometer with an auto-sampler. The temperature was stabilized at 25 °C. Critical parameters include D1 = 8.0 s, AQ = 0.73 s and number of scans = 32. A capillary tube containing 1% trichlorofluoromethane (CCl₃F, 0 ppm) in chloroform was used as internal reference. All reported values are normalized towards the reference. Data analysis was assisted with the software MestRe Nova[®]. Detection of fluoride was performed with ion chromatography (IC) using a Dionex ICS-300C ion chromatograph equipped with an IonPac[®] AS18 analytical column and an ED40 conductivity detector. The scanning electron microscope (SEM) was a Hitachi S-4800 system with a cold field-emission electron source for ultra-high resolution and an energy dispersive X-ray spectrometer (EDXS).

3. Results and discussion

As illustrated by SEM-EDXS in Fig. 1, tin was successfully introduced in the catalyst layer. The existence of SnO₂ and the corresponding oxidation state was also confirmed by X-ray

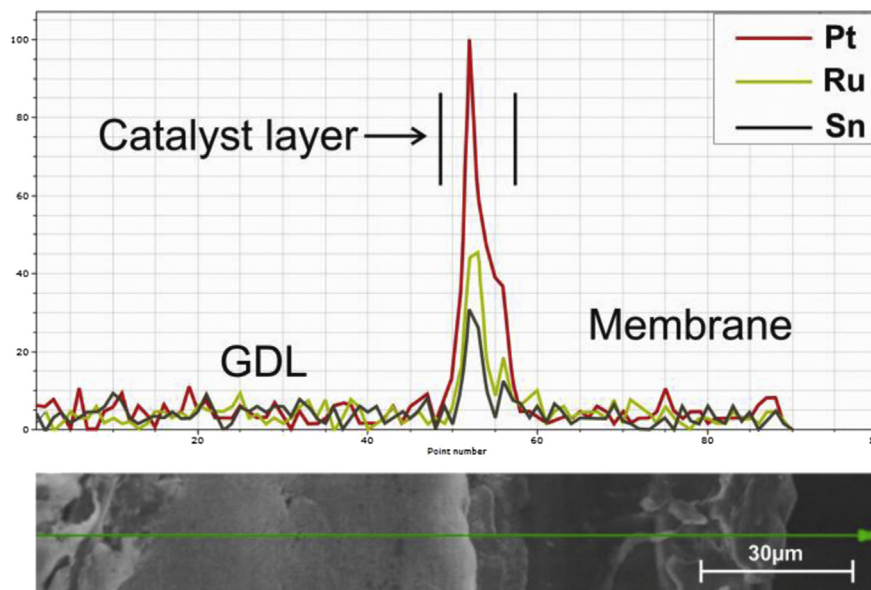


Fig. 1. SEM-EDXS cross section image and atomic line profile of MEA electrode ion exchanged with SnO₂.

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