Boosting Pt oxygen reduction reaction activity by tuning the tin oxide support

Emiliana Fabbri[a,*], Annett Rabis[a], Yuji Chino[b], Makoto Uchida[b], Thomas J. Schmidt[a,c]

[a] Electrochemistry Laboratory, Paul Scherrer Institut, 5232 Villigen-PSI, Switzerland.
[b] Fuel Cell Nanomaterials Center, University of Yamanashi, Kofu 400-0021, Japan
[c] Laboratory of Physical Chemistry, ETH Zürich, 8093 Zürich, Switzerland

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ABSTRACT

The influence of the dopant element on the physicochemical properties of the SnO_2 support and on the oxygen reduction reaction (ORR) activity of the supported Pt nanoparticles was systematically studied. The dopant element and concentration significantly influence the SnO_2 crystal structure and the electrical conductivity, as well as the ORR activity in 0.1 M $HClO_4$ of the supported Pt catalysts. ORR activities significantly exceeding that of Pt deposited on carbon were observed for Pt nanoparticles supported on Nb- and W-doped SnO_2. No linear correlation between the support conductivity and the ORR activity was observed, suggesting that other factors, such as (electronic) metal–support interactions, could play a role in the ORR activity of Pt catalysts supported on metal oxides.

1. Introduction

Durability is currently a challenging issue for polymer electrolyte fuel cells (PEFCs). For transport applications, DOE technical targets for PEFC electrocatalysts aim at a maximum loss in mass activity of 40% in a protocol test that consists in 50,000 cycles at 500 mV s^{-1} between 1 and 1.5 V [1]. This protocol was mostly designed to test the electrochemical stability of the catalyst support at high potentials (such as 1.5 V), to which the PEFC cathode can be exposed during start/stop events. At present, state-of-the-art PEFC cathode catalysts consist of Pt nanoparticles supported on high surface area carbon (Pt/C), which is very prone to oxidization at high potentials, causing loss of mass activity during start/stop events [2]. Therefore, great efforts have been directed towards the development of alternative Pt support materials. Doped SnO_2 is a very interesting support material for Pt electrocatalysts since it combines conductivity, high surface area, and stability under PEFC cathodic operating conditions [3–13]. Improved durability and, at times, higher oxygen reduction reaction (ORR) activity have been observed for Pt catalysts supported on doped SnO_2, compared to Pt/C and/or Pt/SnO_2 [5–8,11,12]. It is often speculated that the dopant mainly enhances the conductivity of the support, leading to better utilization of the Pt catalysts and thus to higher ORR activity. However, an unambiguous correlation between support conductivity and Pt ORR activity has not yet been demonstrated.

In this study, several dopants have been introduced into the SnO_2 lattice using thin-film model electrodes, in order to gain insights into the effect of the dopant element on the physicochemical properties of the SnO_2 support and the ORR activity of the supported Pt nano-catalysts. We can show that the ORR activity of the supported Pt nanoparticles depends significantly on the SnO_2 dopant element and, in the best case, can exceed that of Pt/carbon electrodes by more than a factor of 2.

2. Experimental

Doped SnO_2 thin films (200–300 nm thickness) were deposited as described previously [9,14] on glassy carbon substrates by magnetron sputtering and annealed in N_2 at 400 °C for 2 h. For each dopant, the doping concentration was varied using metal chips incorporated into the Sn target. The electrochemical studies presented here were restricted to doped SnO_2 supports presenting no significant secondary phases in the XRD pattern (Bruker D8), and showing good structural stability. The dopant concentration was determined by Rutherford Backscattering Spectrometry (RBS) measurements, except for Sb–SnO_2 due to the close backscattering energies of Sb and Sn atoms. In the latter case, X-ray photoelectron spectroscopy (XPS) was used. XPS measurements were performed using an ESCALAB 220iXL spectrometer (Thermo Fischer Scientific) equipped with an Al Kα monochromatic X-ray source. The electronic conductivity of the doped SnO_2 films was analyzed by a four-point probe method (FPP 5000 Veeco Instrument).

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2 μg cm^{-2} Pt was deposited onto the doped SnO$_2$ and onto a glassy carbon support (GC/Pt) as described in previous work [9], resulting in 2–10 nm interconnected Pt nanoparticles [9].

Electrochemical measurements were carried out at room temperature in a three-electrode glass cell using a Biologic VMP3 potentiostat. The Hg/Hg$_2$SO$_4$ reference electrode was calibrated vs. the reversible hydrogen electrode (RHE). Initially the electrodes were cycled 20 times at 50 mV s^{-1} between 0.05 and 1.1 V$_{RHE}$ in N$_2$-purged 0.1 M HClO$_4$ (SupraPure, Merck AG). The electrochemically active surface area (ECSA) was determined by a modified hydrogen underpotential deposition (H$_{upd}$) method described elsewhere [15]. For the ORR experiments, polarization curves were recorded in O$_2$-saturated electrolyte in the cathodic scan direction at 5 mV s^{-1} and 1600 rpm and reported after IR correction using impedance spectroscopy. Mass-transport-corrected kinetic currents were derived from the ORR polarization curves using the Koutecky-Levich equation and were normalized to the corresponding ECSA to obtain the specific kinetic ORR current (j$_{spec}$).

3. Results and discussion

Table 1 summarizes the main physicochemical properties of the doped SnO$_2$ thin films, showing how strongly the dopant element and its concentration affect the crystal structure and conductivity. Fig. 1 shows the XRD patterns and the XPS spectra for each doped SnO$_2$ support.

Doping SnO$_2$ with Sb strongly influences the host crystal structure since for the largest Sb concentration an amorphous structure is observed even after the annealing treatment. By contrast, XRD patterns with structures similar to that of SnO$_2$ are achieved for Sb concentrations below 20 at% (Fig. 1a). The conductivity decreases by almost 4 orders of magnitude as the Sb content increases from 9 to 30 at%. Szczuko et al. reported that for low doping levels Sb is mostly present in the SnO$_2$ host lattice as Sb^{5+}. Large dopant concentrations lead to an increase in the number of Sb^{3+} ions, with the Sb^{3+} content even exceeding that of Sb^{5+} for high dopant concentrations (about 30 at%) [16]. The co-presence of Sb^{3+} and Sb^{5+} results in a decrease in conductivity since compensating effects take place, i.e. Sb^{5+} acts as an electron donor while Sb^{3+} behaves as an electron acceptor [17]. The XPS spectra of the Sb3d$_{3/2}$ peak (the Sb3d$_{5/2}$ peak overlaps with that of O1s) show a progressive decrease in the peak maximum binding energy with increasing Sb concentration, indicating a transition from Sb^{5+} to Sb^{3+} (Fig. 1b) [18,19]. The decrease in conductivity with increasing Sb concentration can therefore be rationalized in terms of an increase in the number of Sb^{3+} ions.

The XRD patterns for Nb–SnO$_2$ show all the main peaks related to the SnO$_2$ structure, even though different preferential orientations can be observed depending on the dopant concentration (Fig. 1c). A small peak related to SnO is present for the lowest Nb concentration. The XPS spectra show the Nb3d$_{5/2}$ peak at about 207 eV (Fig. 1d), which corresponds to the presence of Nb^{5+} [20]. The conductivity increases with increasing Nb concentration, reaching its highest measured value of 760 Scm^{-1} for 2.1 at% Nb-SnO$_2$.

Ta–SnO$_2$ films again present the typical SnO$_2$ rutile structure, but with different preferential orientations. An exception is the 7 at% Ta-SnO$_2$, which has an amorphous structure (Fig. 1e). The XPS spectra of the Ta–SnO$_2$ samples show the Ta4d$_{5/2}$ peak at a binding energy of about 230–231 eV (Fig. 1f), indicating incorporation of Ta with a 5 + oxidation state [21]. The conductivity decreases as the Ta concentration increases, reaching a maximum of 650 Scm^{-1} for 1 at% Ta–SnO$_2$.

Finally, W–SnO$_2$ samples show the SnO$_2$ rutile structure, but the intermediate dopant composition exhibits an additional distinct peak corresponding to SnO (Fig. 1g). Furthermore, while the W4f$_{7/2}$ peak maximum is located at ~35.9 eV for the 1.2 and 3 at% W–SnO$_2$, typical of WO$_3$ oxides [22], the W4f$_{7/2}$ peak maximum shifts to smaller binding energies for the 2 at% W-SnO$_2$, indicating reduced W cations (Fig. 1h). The conductivity does not show a linear relationship with W dopant concentration and reaches its maximum value for the 2 at% W–SnO$_2$ sample (150 Scm^{-1}), probably due to the presence of reduced cations in this sample.

Characteristic cyclic voltammograms (CVs) for doped SnO$_2$/Pt and GC/Pt electrodes are shown in Fig. 2. Generally, in the CVs a suppressed H$_{upd}$ region is observed which prevents the assessment of preferential Pt facets as a function of the support. The capacitive current varies significantly depending on the support, probably due to the different capacitive contributions of the doped SnO$_2$ oxides. Table 1 also shows that, despite a constant Pt loading, the ECSA varies strongly depending on the support, the ECSA of doped SnO$_2$/Pt being significantly lower than that of GC/Pt. Differences in Pt nanoparticle morphology as a function of the support could influence the ECSA. However, for the same dopant element different ECSAs can be obtained simply by varying the dopant concentration, indicating that support properties have most likely a strong influence on Pt adsorption properties.

The ORR curves and Tafel plots of the most active sample for each doped SnO$_2$/Pt series and for GC/Pt are shown in Fig. 2f and g, respectively. The highest ORR specific activity determined at 0.9 V$_{RHE}$ is achieved by the 1.7 at% Nb-SnO$_2$/Pt electrode, with a specific activity as high as 710 μA cm$_{Pt}^{-2}$. For comparison, GC/Pt ORR activity is about 270 μA cm$_{Pt}^{-2}$, comparable to that of Pt nanoparticles supported on high surface area carbon [23]. Relatively high ORR activity is also observed for 1.2 at% W–SnO$_2$/Pt, while Pt supported on Ta– and Sb–SnO$_2$ show the lowest, comparable, ORR activity.

Table 1
Summary of the physicochemical properties of the doped SnO$_2$/Pt samples studied, including support structure, dopant concentration, conductivity, and the Pt ECSA. The main properties of the GC/Pt reference sample are also included.

Dopant	Acronyms	Support structure	[Dopant] (at%)	Conductivity (Scm^{-1})	Pt ECSA (m^2 g^{-1})
Sb	9 at% Sb-SnO$_2$	Rutile	9	140	30.5
	20 at% Sb-SnO$_2$	Rutile	20	11	30.4
	30 at% Sb-SnO$_2$	Amorphous	30	0.05	37
Nb	1 at% Nb-SnO$_2$	Rutile	1	100	25
	1.7 at% Nb-SnO$_2$	Rutile	1.7	290	28
	2.1 at% Nb-SnO$_2$	Rutile	2.1	760	32
Ta	1 at% Ta-SnO$_2$	Rutile	1	650	26
	1.8 at% Ta-SnO$_2$	Rutile	1.8	350	29
	3 at% Ta-SnO$_2$	Rutile	3	290	31
	4.2 at% Ta-SnO$_2$	Rutile	4.2	170	35
	7 at% Ta-SnO$_2$	Amorphous	7	0.15	36
W	1.2 at% W-SnO$_2$	Rutile	1.2	130	28
	2 at% W-SnO$_2$	Rutile plus SnO	2	150	27
	3 at% W-SnO$_2$	Rutile	3	15	26
GC		Amorphous	–	220	45