Electrochemical oxidation of methanol on Pt/(Ru$_x$Sn$_{1-x}$)O$_2$

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Abstract: Ru-doped SnO$_2$ powder, (Ru$_x$Sn$_{1-x}$)O$_2$, with a Sn:Ru atomic ratio of 9:1 was synthesized and used as a support for Pt nanoparticles (30 mass % loading). The (Ru$_x$Sn$_{1-x}$)O$_2$ support and the Pt/(Ru$_x$Sn$_{1-x}$)O$_2$ catalyst were characterized by X-ray diffraction measurements, energy dispersive X-ray spectroscopy and transmission electron microscopy (TEM). The (Ru$_x$Sn$_{1-x}$)O$_2$ was found to be a two-phase material consisting of probably a solid solution of RuO$_2$ in SnO$_2$ and pure RuO$_2$. The average Pt particle size determined by TEM was 5.3 nm. Cyclic voltammetry of Pt/(Ru$_x$Sn$_{1-x}$)O$_2$ indicated good conductivity of the support and displayed the usual features of Pt. The results of the electrochemical oxidation of CO$_{\text{ads}}$ and methanol on Pt/(Ru$_x$Sn$_{1-x}$)O$_2$ were compared with those on commercial Pt/C and PtRu/C catalysts. Oxidation of CO$_{\text{ads}}$ on Pt/(Ru$_x$Sn$_{1-x}$)O$_2$ starts at lower positive potentials than on PtRu/C and Pt/C. Potentiodynamic polarization curves and chronoamperometric curves of methanol oxidation indicated higher initial activity of the Pt/(Ru$_x$Sn$_{1-x}$)O$_2$ catalyst compared to PtRu/C, but also a greater loss in current density over time. A potentiodynamic stability test of the catalysts revealed that deactivation of Pt/(Ru$_x$Sn$_{1-x}$)O$_2$ and Pt/C was primarily caused by poisoning of the Pt surface by residues of methanol oxidation, which mostly occurred during the first potential cycle. In the case of PtRu/C, the poisoning of the surface was minor and deactivation was caused by surface area loss of the PtRu.

Keywords: methanol oxidation, CO oxidation, platinum, Ru-doped SnO$_2$, electrocatalysis, fuel cell.

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INTRODUCTION

Anode and cathode catalysts currently used for polymer electrolyte membrane fuel cells (PEMFCs) are Pt or Pt-alloy nanoparticles supported on carbon blacks. The role of the support for the catalysts is to provide a physical surface for a fine dispersion of catalyst particles, necessary to achieve a high surface area. To be efficient, the support also needs to have high surface area, preferably mesoporous structure, high electrical conductivity and high stability under fuel cell operating conditions. The main drawback of carbon blacks, as well as other carbon materials (carbon fibers, carbon nanotubes, graphene), is their insufficient corrosion resistance. Although the problem of instability of the supporting material is more prominent for a cathode catalyst because of its higher potential and the presence of $\text{H}_2\text{O}_2$ as a by-product of oxygen reduction, an anode catalyst could also be exposed to much more oxidative conditions in the case of cell reversal caused by fuel starvation. Partial oxidation of the carbon induces the formation of oxygen-containing functional groups on the surface that weaken bonding with Pt nanoparticles, thus promoting surface diffusion of Pt nanoparticles and their agglomeration. If the carbon support is oxidized to CO or CO$_2$, Pt nanoparticles are detached from the surface. In both cases, the final result is a decrease in the electrochemically active surface area of Pt. This problem has initiated a lot of research in the last few years aimed at finding an appropriate replacement for carbon supports. Ceramic materials, such as metal oxides and carbides, distinguish themselves as promising candidates not only due to their high stability in a fuel cell environment, but also because of their possible interaction with the deposited metal particles, which could result in a promotion of the activity of the catalyst.

Metal oxides are electric insulators at the operating temperatures of PEMFCs. However, sub-stoichiometric oxides, oxides doped with a foreign metal and nanostructured oxides, especially those of titanium, tin and tungsten, are found to have acceptable conductivity for application as a support for electrocatalysts. When using as an anode catalyst in a direct methanol or ethanol fuel cell (DMFC, DEFC), the metal-oxide support can also serve as a co-catalyst to Pt nanoparticles, providing them with oxygen-containing species at lower electrode potentials.

The state-of-the-art anode catalyst in DMFC is a Pt–Ru nanoalloy. It is accepted that the methanol oxidation reaction (MOR) commences earlier on Pt–Ru than on Pt due to the bi-functional mechanism, according to which oxophilic Ru sites readily adsorb oxygen-containing species, which react with carbonaceous species formed by methanol adsorption on the Pt sites. Pt–Sn alloys were also investigated for the MOR, but found to be inactive. Interestingly, good activity was observed for electrosorbed Sn on Pt. It was also reported that tin oxide promotes the MOR on Pt, as shown for Pt microparticles dispersed on SnO$_2$ thin
films and polycrystalline Pt partially covered by SnO₂ nanoparticles. SnO₂ doped by Sb was investigated as a support for Pt nanoparticles. It was concluded that Sb-doped SnO₂ promotes methanol and ethanol oxidation and stabilizes the Pt nanoparticles in the fuel cell.

In the present study, Pt nanoparticles supported on SnO₂ doped with RuO₂ were prepared. RuO₂ as a dopant should increase the electrical conductivity of SnO₂ and, together with SnO₂, provide oxygen-containing species necessary for efficient methanol oxidation on Pt. The supporting material, labeled as (RuₓSn₁₋ₓ)O₂, and the catalyst Pt/(RuₓSn₁₋ₓ)O₂ were characterized by the X-ray diffraction technique (XRD), transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS). The catalyst was tested for electrochemical oxidation of CO and methanol and its performance was compared to those of commercial Pt/C and PtRu/C catalysts.

**EXPERIMENTAL**

*Synthesis of the support and the catalyst*

The RuₓSn₁₋ₓO₂ supporting particles were prepared as follows. A solution 5.3 g of SnCl₄·5H₂O, 0.98 g of RuCl₃·xH₂O (35–45 mass % Ru), 2.5 mL of HCl and 40 mL of high purity water (Millipore, 18 MΩ cm resistivity) was prepared and mixed to homogeneity. The mixture is added dropwise in 50 mL of a 34 % aqueous solution of hydrazine at room temperature. Then, the solution was refluxed for 10 days. Subsequently, the formed precipitate was repeatedly rinsed with water and centrifuged until the supernatant was free of Cl⁻. The resulting product was dried in air for 24 h at 120 °C and heated at 400 °C for 2 h.

The Pt nanoparticles were deposited on the RuₓSn₁₋ₓO₂ support by a modified borohydride reduction method. RuₓSn₁₋ₓO₂ powder was dispersed in water in an ultrasonic bath. Then H₂PtCl₆ aqueous solution was added into dispersion under continuous stirring. The metal salt was reduced with excess of sodium borohydride. The precipitate was rinsed with water and dried at 80 °C.

*Physicochemical characterization*

Adsorption and desorption isotherms of N₂ were measured on RuₓSn₁₋ₓO₂ support at –196°C, using the gravimetric McBain method. The BET specific surface area, S_BET, and pore size distribution were calculated from the isotherms. Pore size distribution was estimated by applying the BJH method to the desorption branch of the isotherms.

Phase composition of the (RuₓSn₁₋ₓ)O₂ support was investigated by XRD technique. Siemens D-500 diffractometer was employed with CuKα radiation of wavelength 0.154056 nm in conjunction with a CuKα nickel filter.

Elemental analysis of the (RuₓSn₁₋ₓ)O₂ support and the Pt/RuₓSn₁₋ₓO₂ catalyst was performed by EDS analysis using a scanning electron microscope Tescan VEGA TS 5130MM coupled with an EDS system INCA PentaFET-x3, Oxford Instruments.

The Pt/(RuₓSn₁₋ₓ)O₂ catalyst was characterized for morphology, particle size distribution and chemical composition by TEM. The sample was sonicated in ethanol and a drop of the suspension was placed on copper grid (300 mesh) covered with a lacy carbon film and dried in air. A combination of high angle annular dark field scanning transmission electron microscopy (HAADF, STEM) and electron energy loss spectroscopy (EELS) was applied. HAADF was chosen because of its strong correlation between atomic number and image intensity,
making it very easy to distinguish between heavy elements, such as Pt, and light supports, such as \((\text{Ru}_x\text{Sn}_{1-x})\text{O}_2\) particles. The measurements were performed on TEAM0.5 transmission electron microscope with corrected aberration operated at 80 kV. EDS analysis was performed on TEM microscope CM200-FEG operating at 400 kV using an Oxford Instruments EDS system with INCA software. Crystallographic information from individual Pt particles was obtained by numerical Fourier filtering (FFT, fast Fourier transformation) of the digital image intensity spectra. All TEM characterization was realized at the National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, CA.

**Electrochemical characterization**

For the electrochemical characterization, the Pt/(Ru\(_x\)Sn\(_{1-x}\))O\(_2\) catalyst was applied on a glassy carbon (GC) substrate in the form of a thin-film.\(^1\) The GC electrode (Tacussel rotating disk electrode, 5 mm in diameter) was polished with Al\(_2\)O\(_3\) slurry and washed ultrasonically with water before use. The ink was made by mixing of 4 mg of Pt/(Ru\(_x\)Sn\(_{1-x}\))O\(_2\) powder with 1 cm\(^3\) of high purity water and 50 \(\mu\)L of Nafion\(^\circledR\) solution (5 wt. %, 1100 E.W., Aldrich). After 1 h of agitation in an ultrasonic bath, 10 \(\mu\)L of the suspension was placed onto the GC electrode and left to dry overnight. This procedure of film preparation gave 60 \(\mu\)g of Pt per cm\(^2\) of the GC surface.

Electrochemical characteristics of the Pt/(Ru\(_x\)Sn\(_{1-x}\))O\(_2\) thin film were investigated by cyclic voltammetry in 0.10 M H\(_2\)SO\(_4\) saturated with N\(_2\). After immersion into the electrolyte, the electrode was subjected to 15 potential cycles between 0.04 and 1.2 V at a scan rate of 100 mV s\(^{-1}\). The oxidation of CO\(_{\text{ads}}\) was examined in the same electrolyte after adsorbing CO at 0.1 V for 30 min and replacing CO by a N\(_2\) atmosphere.

The MOR was investigated in an electrolyte containing 0.5 M CH\(_3\)OH. Upon oxidation of CO\(_{\text{ads}}\), the electrode potential was held at 0.1 V, methanol was added into the electrolyte and after 2 min a linear sweep at 50 mV s\(^{-1}\) (potentiodynamic polarization curve) or potential step at 0.5 V vs. RHE (chronoamperometric experiment) was applied.

As reference electrocatalysts, a sample of Pt nanoparticles supported on XC-72R carbon with a loading of 20 mass % of Pt (Pt/C) and a sample of PtRu nanoparticles supported on the same carbon with a loading of 20 mass % of PtRu (PtRu/C), both of them manufactured by E-Tek, were used. The average diameters of Pt and PtRu particles were 2.5\(^1\) and 2.7 nm,\(^2\) respectively. The metal loading on the electrode was 20 \(\mu\)g cm\(^{-2}\) for both Pt/C and PtRu/C.

The electrochemically active surface area of Pt and PtRu were determined from the charge of the CO\(_{\text{ads}}\) oxidation as well as from the charge of the oxidation of underpotentially deposited Cu.\(^3\) Cu was deposited from a supporting electrolyte containing 2 mM CuSO\(_4\) at a potential of 0.33 V. A three-compartment electrochemical glass cell was used with a Pt wire as the counter electrode and a saturated calomel electrode as the reference electrode. All the potentials reported in the paper are expressed on the scale of the reversible hydrogen electrode (RHE). A Pine RDE4 potentiostat and Philips PM 8143 X–Y recorder were used. All the measurements were performed at 25 °C.

**RESULTS AND DISCUSSION**

**Physicochemical characterization**

Analysis of N\(_2\) adsorption and desorption isotherms revealed that the (Ru\(_x\)Sn\(_{1-x}\))O\(_2\) powder had a BET surface area of 141 m\(^2\) g\(^{-1}\) and mesoporous structure with pores radii mostly between 2 and 3 nm.
Both SnO$_2$ and RuO$_2$ crystallized in the tetragonal rutile structure with similar lattice constants (SnO$_2$: $a = 0.47382$ nm, $c = 0.31871$ nm; RuO$_2$: $a = 0.44994$ nm, $c = 0.31071$ nm). The ionic radii of Sn(IV) and Ru(IV) of 0.083 and 0.076 nm are similar enough to enable the formation of a substitutional solid solution, designated as (Ru$_x$Sn$_{1-x}$)O$_2$. The experimental XRD pattern for the (Ru$_x$Sn$_{1-x}$)O$_2$ support and the reference spectra of RuO$_2$ and SnO$_2$, taken from the corresponding JCPD cards, are shown in Fig. 1. The pattern for (Ru$_x$Sn$_{1-x}$)O$_2$ features overlapping peaks for SnO$_2$ and RuO$_2$. The 2$\theta$ peak positions and corresponding reflections for SnO$_2$ could be identified as 26.6° (110); 33.8° (101); 37.9° (200) 51.7° (211) and 64.7° (112) and for RuO$_2$ as 28.0° (110), 35.0° (101) and 54.2° (211). Such an XRD microstructure analysis suggests that (Ru$_x$Sn$_{1-x}$)O$_2$ consisted of two separate phases. Taking into account the possibility of the formation of a solid solution and greater amount of SnO$_2$, it could be suggested that the two phases detected by XRD were a solid solution of RuO$_2$ in SnO$_2$ and pure RuO$_2$.

![Fig. 1. XRD Pattern for the Pt/(Ru$_x$Sn$_{1-x}$)O$_2$ catalyst. The 2$\theta$ positions for bulk SnO$_2$ and RuO$_2$ are shown in the plot for reference.](image-url)
EDS analysis revealed that the atomic ratio of Sn:Ru in the \((\text{Ru}_x\text{Sn}_{1-x})\text{O}_2\) powder as well as in \(\text{Pt}/(\text{Ru}_x\text{Sn}_{1-x})\text{O}_2\) was 9:1. This shows that during the deposition of Pt nanoparticles on the \((\text{Ru}_x\text{Sn}_{1-x})\text{O}_2\) support, its composition remained unchanged. The Pt loading of \(\text{Pt}/(\text{Ru}_x\text{Sn}_{1-x})\text{O}_2\) was found to be 30 mass %.

HAADF images of the Pt particles and the \((\text{Ru}_x\text{Sn}_{1-x})\text{O}_2\) particle clusters are presented in Fig. 2a. It can be seen that Pt was unevenly distributed in the form of separate particles and particle clusters. The histogram given in Fig. 2b indicates the log–normal distribution of Pt particle size with an average size of 5.3 nm. Pt particles were mostly located near \((\text{Ru}_x\text{Sn}_{1-x})\text{O}_2\) particle clusters, as presented in Fig. 2c and d, owing to the ability of SnO\(_2\) to act as a nucleation agent. EELS analysis of the \((\text{Ru}_x\text{Sn}_{1-x})\text{O}_2\) clusters revealed the presence of elemental Sn besides SnO\(_2\). It could be assumed that Sn(IV) ions were partially reduced during Pt deposition by the borohydride reduction method.

Fig. 2. TEM Images of the Pt/(\text{Ru}_x\text{Sn}_{1-x})\text{O}_2\) catalyst: a) HAADF image of the Pt particles and \((\text{Ru}_x\text{Sn}_{1-x})\text{O}_2\) particle clusters, b) histogram of Pt particle size distribution, c) and d) close-up HAADF images of Pt particles close to \((\text{Ru}_x\text{Sn}_{1-x})\text{O}_2\) particle clusters.

**Cyclic voltammetry and CO\(_{\text{ads}}\) oxidation**

The voltammograms of CO\(_{\text{ads}}\) stripping recorded on Pt/(\text{Ru}_x\text{Sn}_{1-x})\text{O}_2, PtRu/C and Pt/C, as well as the first cyclic voltammograms after CO\(_{\text{ads}}\) stripping, are
shown in Fig. 3. The voltammograms after stripping of the CO\textsubscript{ads} showed complete oxidation of the CO\textsubscript{ads} and displayed the surface characteristics of the electrodes. The CO\textsubscript{ads} stripping charge was used for the determination of the electrochemically active surface area (EASA) of Pt (in the case of Pt/(Ru\textsubscript{x}Sn\textsubscript{1-x})O\textsubscript{2} and Pt/C) and PtRu (in the case of PtRu/C); hence, the current densities in Fig. 3 were normalized with respect to the EASA. It should be noted that the EASA values determined by the oxidation of underpotentially deposited monolayer of Cu (not shown) were the same, within experimental error, as those determined by oxidation of CO\textsubscript{ads}.

The cyclic voltammogram of Pt/(Ru\textsubscript{x}Sn\textsubscript{1-x})O\textsubscript{2} given in Fig. 3a shows well defined peaks for hydrogen adsorption/desorption and Pt-oxide formation/reduction that are characteristics of clean polycrystalline Pt. The high currents in the
so-called double-layer region of Pt can be mainly ascribed to the pseudo-capacitive behavior of the \((\text{Ru}_x\text{Sn}_{1-x})_2\)O support. The voltammogram is well centered and without inclination, demonstrating good conductivity of the \((\text{Ru}_x\text{Sn}_{1-x})_2\)O support.

Fig. 3a shows that \(\text{CO}_{\text{ads}}\) oxidation on Pt/(\(\text{Ru}_x\text{Sn}_{1-x})_2\)O occurred from 0.35 to 0.8 V. At low potentials, an anodic wave with a maximum at 0.43 V was observed. The main peak is a superposition of two peaks with maxima positioned at 0.70 and 0.72 V. Contrary to Pt/(\(\text{Ru}_x\text{Sn}_{1-x})_2\)O, the voltammograms of the oxidation of \(\text{CO}_{\text{ads}}\) on PtRu/C (Fig. 3b) and Pt/C (Fig. 3c) showed single peaks. This suggested that the complex structure of the \(\text{CO}_{\text{ads}}\) oxidation voltammogram on Pt/(\(\text{Ru}_x\text{Sn}_{1-x})_2\)O was related to the presence of SnO\(_2\). Indeed, a profile of \(\text{CO}_{\text{ads}}\) stripping with three peaks at almost the same potentials as those for Pt/(\(\text{Ru}_x\text{Sn}_{1-x})_2\)O was reported recently for Pt\(_3\)Sn/C catalyst containing Sn in the form of SnO\(_2\). On Pt\(_3\)Sn bulk alloy, it was also found that the \(\text{CO}_{\text{ads}}\) stripping begins at 0.25 V, but most of the \(\text{CO}_{\text{ads}}\) is oxidized in the second anodic wave starting at 0.68 V with the peak at about 0.75 V. The authors assumed that a unique state of \(\text{CO}_{\text{ads}}\) existed on the Pt\(_3\)Sn surface, which is only formed at high coverage with an adsorption energy lower than that for pure Pt. Therefore, the first anodic wave in Fig. 3a could be ascribed to the oxidation of weakly bound \(\text{CO}_{\text{ads}}\) on the Pt sites directly contacting SnO\(_x\), while the main peak corresponds to the oxidation of strongly bound \(\text{CO}_{\text{ads}}\). The splitting of this peak might reflect \(\text{CO}_{\text{ads}}\) oxidation on Pt sites directly contacting SnO\(_x\) and the reaction on Pt sites completely surrounded by other Pt atoms. Comparing the \(\text{CO}_{\text{ads}}\) oxidation on Pt/(\(\text{Ru}_x\text{Sn}_{1-x})_2\)O to that on PtRu/C and Pt/C, the lowest onset potential on Pt/(\(\text{Ru}_x\text{Sn}_{1-x})_2\)O suggests that this catalyst should exhibit high CO tolerance.

**Methanol oxidation**

The activity of the catalysts for the MOR was first tested under potentiodynamic conditions. The polarization curves recorded in the positive going sweeps over 250 potential cycles are displayed in Fig. 4. The voltammograms recorded in the supporting electrolyte are also displayed. The Pt/(\(\text{Ru}_x\text{Sn}_{1-x})_2\)O catalyst features remarkably high current densities in the first potential cycle compared to Pt/C and especially to PtRu/C. Hydrogen desorption peaks were not attenuated, indicating that the electrocatalysts were not poisoned by the product of the dissociative adsorption of methanol during a 2-min potential hold at 0.1 V. However, already in the second cycle, the onset potential of the MOR on Pt/(\(\text{Ru}_x\text{Sn}_{1-x})_2\)O and Pt/C had shifted positively, probably as a consequence of poisoning of the Pt surface, which was evidenced by suppression of the hydrogen desorption peaks. Although the maximum current density on Pt/(\(\text{Ru}_x\text{Sn}_{1-x})_2\)O did not change with potential cycling, the activity at low potentials relevant for the operation of the anode in PEMFC was reduced. On the other hand, the activity of PtRu/C in the
first cycle was much lower than the activity of Pt/(Ru\textsubscript{x}Sn\textsubscript{1-x})O\textsubscript{2} and Pt/C, but without significant loss of activity over the applied 250 potential cycles.

Fig. 4. Potentiodynamic polarization curves for the MOR recorded on a) Pt/(Ru\textsubscript{x}Sn\textsubscript{1-x})O\textsubscript{2}, b) Pt/C and c) PtRu/C in 0.1 M H\textsubscript{2}SO\textsubscript{4} containing 0.5 M CH\textsubscript{3}OH at a rate of 50 mV s\textsuperscript{-1} over 250 potential cycles. Anodic parts of the cyclic voltammograms recorded in 0.1 M H\textsubscript{2}SO\textsubscript{4} before the addition of CH\textsubscript{3}OH are also presented (dash line).

High activity of Pt/(Ru\textsubscript{x}Sn\textsubscript{1-x})O\textsubscript{2} in the first cycle as well as the lower onset potential of CO\textsubscript{ads} oxidation on this catalyst (Fig. 3a) compared to Pt/C and PtRu/C could be ascribed to SnO\textsubscript{x} and its donation of oxygen-containing species. A recent investigation of CO and methanol oxidation on Pt partially covered by SnO\textsubscript{2} nanoparticles\textsuperscript{9,21} showed that the lattice oxygen from Sn(II)O rather than Sn(IV)O is active in the oxidation of CO and methanol. This could suggest an explanation for the sharp drop in the activity for the MOR after the first cycle. Namely, during the 2 min potential hold at 0.1 V prior to the potential cycling experiment, the Sn(IV) ions in (Ru\textsubscript{x}Sn\textsubscript{1-x})O\textsubscript{2} could be partially reduced to Sn(II) ions. If the partial reduction of Sn(IV) ions is a slow process, there is not enough time to form Sn(II) ions in the following continuous cycles.

The chronoamperometric test of Pt/(Ru\textsubscript{x}Sn\textsubscript{1-x})O\textsubscript{2} and PtRu/C was performed at 0.50 V for 25 min. Similar to the findings of the potentiodynamic experiments, the chronoamperometric results (Fig. 5) confirmed the higher activity of the PtRu catalyst, but the difference in the activity between Pt/(Ru\textsubscript{x}Sn\textsubscript{1-x})O\textsubscript{2} and PtRu/C slightly decreased during the experiment.
Fig. 5. Chronoamperometric curves of the MOR recorded on Pt/(Ru<sub>x</sub>Sn<sub>1-x</sub>)O<sub>2</sub> and PtRu/C catalysts in 0.1 M H<sub>2</sub>SO<sub>4</sub> containing 0.5 M CH<sub>3</sub>OH at a constant potential 0.50 V.

**Stability of the catalysts**

The activity of the catalysts for the MOR could deteriorate over time because of a gradual poisoning of the Pt surface by the methanol oxidation residues and/or because of a loss of the electrochemically active surface area. In order to resolve which effect was predominant, all three catalysts were subjected to potential cycling in the supporting electrolyte containing no methanol. At the beginning and at the end of the experiment, the procedure for CO adsorption was employed in order to determine the EASA. Additionally, for the Pt/(Ru<sub>x</sub>Sn<sub>1-x</sub>)O<sub>2</sub> catalyst, the EASA was continuously monitored by the changes in the hydrogen adsorption/desorption peaks. The changes in the Pt/(Ru<sub>x</sub>Sn<sub>1-x</sub>)O<sub>2</sub> cyclic voltammograms over 250 cycles are presented in Fig. 6. The currents in the hydrogen adsorption/desorption region as well as in the Pt-oxide formation/reduction region gradually decreased, revealing a loss of EASA. Degradation of Pt under the potentiodynamic conditions could be explained by two mechanisms; surface diffusion of low-coordinated Pt atoms<sup>22</sup> and electrochemical dissolution of Pt,<sup>23–25</sup> either as the direct electro-oxidation of Pt to soluble Pt<sup>2+</sup> (mostly for particles smaller than 4 nm) or as dissolution from the oxide (larger particles).

It should be stressed that the voltammetric currents in the double-layer region, ascribed to pseudo-capacitive currents of the (Ru<sub>x</sub>Sn<sub>1-x</sub>)O<sub>2</sub> support (Fig. 6), do not change during potential cycling. Moreover, the characteristic shape of the voltammogram of CO<sub>ads</sub> oxidation (Fig. 3a), which was related to the presence of SnO<sub>x</sub> in the catalyst, was maintained over the potential cycling. The same shape of the CO<sub>ads</sub> stripping curve before and after the stability test under the poten-
tiodynamic conditions was also reported for Pt$_3$Sn/C catalyst with Sn in a form SnO$_2$. These results indicate that (Ru$_x$Sn$_{1-x}$)O$_2$ is a stable material and suitable for use as a catalyst support.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{cyclic_voltammograms.png}
\caption{Cyclic voltammograms of the Pt/(Ru$_x$Sn$_{1-x}$)O$_2$ catalyst recorded in 0.1 M H$_2$SO$_4$ at a scan rate of 50 mV s$^{-1}$ over 250 cycles.}
\end{figure}

The EASA and the methanol oxidation current density for the Pt/(Ru$_x$Sn$_{1-x}$)O$_2$ catalyst collected over 250 potential cycles are shown in Fig. 7. The EASA data were determined from the hydrogen adsorption/desorption charge in all the cycles and from the CO$_{ads}$ oxidation at the beginning and the end of the experiment. The values obtained by these two methods correspond to each other within experimental error. The current densities for the MOR were taken from the potentiodynamic curves in Fig. 4 at a constant potential of 0.50 V. They were calculated using the EASA at the beginning of the experiment. Both the EASA and the methanol oxidation current densities given in Fig. 7 were normalized with respect to their initial values. The results showed that 80 % of the initial activity for the MOR was lost while the EASA decreased by 32 %.

The results of the EASA and the MOR activity loss determined on all three catalysts are summarized in Table I. It is clear that the deactivation of the Pt/(Ru$_x$Sn$_{1-x}$)O$_2$ and Pt/C catalysts was primarily caused by the poisoning of the Pt surface by the methanol oxidation residues, mostly occurring during the first potential cycle (Fig. 4). Contrary to these two catalysts, for PtRu/C the loss of EASA and MOR activity were quite similar, indicating that poisoning of the PtRu nanoparticles was minor. Therefore, it seems that mixing of Pt and Ru at
the atomic level in necessary to achieve high and long-term resistance to poisoning by \( \text{CO}_{\text{ads}} \).

![Graph showing current densities for the MOR and EASA values during potential cycling of Pt/(Ru\(_x\)Sn\(_{1-x}\))O\(_2\) in 0.1 M H\(_2\)SO\(_4\) with and without 0.5 M CH\(_3\)OH. Both types of data are normalized to their initial values. EASA values were calculated from hydrogen desorption charge (bold symbols) and from \( \text{CO}_{\text{ads}} \) oxidation (open symbols). The results of two independent experiments are shown.]

![Table 1. Decrease in the activity for the MOR and the EASA values of the three investigated catalysts, determined during 250 potential cycles in 0.1 M H\(_2\)SO\(_4\) solution with and without the addition of 0.5 M CH\(_3\)OH.]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>MOR Activity loss, %</th>
<th>EASA Loss, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/(Ru(<em>x)Sn(</em>{1-x}))O(_2)</td>
<td>80</td>
<td>32</td>
</tr>
<tr>
<td>Pt/C</td>
<td>70</td>
<td>18</td>
</tr>
<tr>
<td>PtRu/C</td>
<td>30</td>
<td>24</td>
</tr>
</tbody>
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**Prospects for the Pt/(Ru\(_x\)Sn\(_{1-x}\))O\(_2\) catalyst**

The study of Pt/(Ru\(_x\)Sn\(_{1-x}\))O\(_2\) catalyst demonstrated that (Ru\(_x\)Sn\(_{1-x}\))O\(_2\) is stable within the potential range that might be encountered during the operation of a DMFC. This characteristic, as well as good conductivity, makes this oxide material suitable for application as a catalyst support.

The action of (Ru\(_x\)Sn\(_{1-x}\))O\(_2\) as co-catalyst is excellent in short time after running the MOR. However, very soon Pt/(Ru\(_x\)Sn\(_{1-x}\))O\(_2\) looses its high initial activity and the current densities for the MOR drop to 60 % of those attained on the commercial PtRu/C catalyst. Since the experiments show that (Ru\(_x\)Sn\(_{1-x}\))O\(_2\) cannot be an active co-catalyst to Pt over long-term operation, in further impro-
vement of the MOR catalyst without high area carbon as the support, PtRu nanoparticles could be deposited on a (Ru$_x$Sn$_{1-x}$)O$_2$ support.

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REFERENCES