

# Methanol oxidation by pEDOT-pSS/PtRu in DMFC

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## Abstract

Direct methanol fuel cells (DMFCs) are attracting more and more attention because of their operating temperature and easy fuel management. While carbons are the most widely used supports for both metal catalysts, i.e. PtRu for methanol oxidation and Pt for oxygen reduction, conducting polymers also can act as suitable supports for catalyst particles because of their conductive and stable three-dimensional structure. We thus chemically synthesized poly(3,4-ethylenedioxythiophene)-polystyrene-4-sulfonate (pEDOT-pSS) with different (3,4-ethylenedioxythiophene):styrene-4-sulfonate (EDOT:SS) molar ratios and prepared the electrocatalytic systems pEDOT-pSS/PtRu and pEDOT-pSS/Pt, the former by both electrochemical and chemical deposition of PtRu and the latter by chemical deposition of Pt. The results of the electrocatalytic activity tests of the pEDOT-pSS/PtRu composite electrodes performed in 0.1 M H<sub>2</sub>SO<sub>4</sub>–0.5 M CH<sub>3</sub>OH liquid solution and in passive, air-breathing DMFC configuration with Nafion<sup>®</sup> 115 protonic membrane and 1 M CH<sub>3</sub>OH are reported and discussed.

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**Keywords:** Conducting polymers; Methanol oxidation; Passive DMFC; pEDOT-pSS; PtRu catalyst

## 1. Introduction

Direct methanol fuel cells (DMFCs) are very attractive energy conversion systems [1,2] and interest in passive DMFCs for portable applications is increasing [3]. The catalysts of choice in DMFCs, which operate at medium–low temperature, are PtRu for methanol oxidation and Pt for oxygen reduction and are generally supported on carbon, for better metal particle dispersion, despite the recent debate on carbon corrosion. Yet, given their conductive and stable three-dimensional structure, conducting polymers also can act as suitable supports for catalyst particles [4]. Indeed, conducting polymers that host Pt have already been investigated for oxygen reduction [5–11] as well as for methanol oxidation [12–19] even if it is well recognized that Pt alone is poisoned by CO and only a few studies have been performed on conducting polymers hosting PtRu [6,14,20–22], particularly on poly(3,4-ethylenedioxythiophene)-polystyrene-4-sulfonate (pEDOT-pSS) [6]. It has also been demonstrated that pEDOT-pSS is a good electronic–ionic mixed conductor [23]; the combination of electronic and ionic properties of such a polymer in the same potential range in which DMFCs operate

is indeed an important feature for its use as catalyst support in such fuel cells, assuring fast electronic transport and facilitating proton movement. Furthermore, pEDOT-pSS is recognized as one of the most stable conducting polymers, so that its use instead of carbon may be of benefit in terms of electrocatalytic performance stability.

We thus chemically synthesized different pEDOT-pSS composites and prepared pEDOT-pSS/PtRu by both electrochemical and chemical deposition of PtRu and pEDOT-pSS/Pt only by chemical deposition of Pt with a view to passive DMFC assembly. The results of catalytic activity tests of composite pEDOT-pSS/PtRu electrodes in 0.1 M H<sub>2</sub>SO<sub>4</sub>–0.5 M CH<sub>3</sub>OH liquid solution as well as of tests in passive, air-breathing DMFC configuration with Nafion<sup>®</sup> 115 membrane and 1 M CH<sub>3</sub>OH are reported and discussed, the latter also compared to those of passive DMFCs with catalysts supported on Vulcan carbon.

## 2. Experimental

### 2.1. pEDOT-pSS syntheses

Chemical syntheses of pEDOT-pSS composites were carried out at room temperature in aqueous solutions (MQ water, 18.2 MΩ cm, from Millipore Simplicity 185) with different

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EDOT (Aldrich, 99.7%): SS (from NapSS, Aldrich MW = 70,000) molar ratios using  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Fluka, >98%) as oxidant in a 10:1 ratio with the monomer. Here we report the results of pEDOT-pSS composites with a EDOT:SS molar ratios 1:1 (D samples) and 1:2 (E samples). These composites appeared coarse, crystal-like and hard to shatter so they were first ground in a mortar and then in agate jar before powder characterization and electrode preparation.

## 2.2. PtRu and Pt depositions

PtRu deposition on pEDOT-pSS was both electrochemically and chemically achieved. The electrochemical deposition of PtRu was performed on pEDOT-pSS electrodes (see below) in a 0.02 M  $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$  (Fluka, 38% Pt)–0.02 M  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  (Aldrich, 99.98%, 41.3% Ru) solution by polarizing the electrodes for 5 s at  $-58$  mV versus NHE followed by 30 s at open circuit voltage; the steps were repeated until the desired electrodeposition charge was reached. The chemical deposition of PtRu was performed on D pEDOT-pSS powder later [6] by mixing pEDOT-pSS,  $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$  and  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  in suitable ratios with the addition of formaldehyde (Sigma Aldrich, 37% in water) in excess. After a few hours, the product was filtered, washed with MQ water and dried under vacuum overnight at  $70^\circ\text{C}$ . Two samples of pEDOT-pSS/PtRu were prepared with Pt content of 17 and 27 wt%, respectively, as experimentally determined after mineralization of the powder by the tin (II) chloride colorimetric method [24]. The deposition of Pt was performed on D pEDOT-pSS powder by chemical reduction of  $\text{H}_2\text{PtCl}_6$  on pEDOT-pSS with formaldehyde in excess as in Ref. [5], and the Pt content was 22 wt%.

## 2.3. Electrode preparation

Four types of electrode preparations were performed using carbon paper (CP) current collectors (Spectracarb 2050, Spectracorp, USA, 1 mm thick, CP<sub>S</sub> and Hydro2Power, Italy, 0.3 mm thick, CP<sub>H</sub>). For the first type, an aqueous slurry containing 85–80 wt% pEDOT-pSS and 15–20 wt% Teflon<sup>®</sup> (Dupont, 60% aqueous emulsion) was spread onto CP in which Kapton<sup>®</sup> (Dupont) adhesive tape was used to delimit a  $1\text{ cm}^2$  area. These electrodes had pEDOT-pSS loadings from 0.5 to  $4\text{ mg cm}^{-2}$  and were used as support for electrochemical deposition of PtRu. For the second type, a 10 wt% Teflon<sup>®</sup> (Dupont, 60% aqueous emulsion) was added to pEDOT-pSS/PtRu powder suspended in a small amount of MQ water and the slurry spread onto CP supports in a  $1\text{ cm}^2$  delimited area to reach pEDOT-pSS/PtRu loadings from 0.85 to  $1.6\text{ mg cm}^{-2}$ . For the third, a 2-propanol-based ink (without Nafion<sup>®</sup> added) of pEDOT-pSS was sprayed onto  $1\text{ cm}^2$  CP electrodes; the pEDOT-pSS loadings were ca.  $1\text{ mg cm}^{-2}$ . For the fourth type, two 2-propanol-based inks (without Nafion<sup>®</sup>) of pEDOT-pSS/PtRu and of pEDOT-pSS/Pt were sprayed onto  $4\text{ cm}^2$  CP electrodes for DMFC assembly. A small amount of a 1 wt% of Nafion<sup>®</sup> solution in water was sprayed on top of the electrodes just before hot pressing them onto Nafion<sup>®</sup> membrane for better adhesion in MEA preparation.

## 2.4. Powder and electrode characterization

The structural and morphological characterizations of powders and electrodes were done by X-ray diffraction (XRD) and by scanning electron micrograph (SEM); particle size was determined by a laser analyzer and the electronic resistivity by the four-point probe technique. The electrochemical characterization of the pEDOT-pSS electrodes by cyclic voltammetry (CV) was done at  $20\text{ mV s}^{-1}$  in 0.1 M  $\text{H}_2\text{SO}_4$ ; impedance spectroscopy measurements in three-electrode mode at 442 mV versus normal hydrogen electrode (NHE) in the 100 kHz to 100 MHz frequency range, with 5 mV ac perturbation and 10 points per decade acquisition were carried out to evaluate the intrinsic ionic conductivity of the polymer at room temperature in  $\text{H}_2\text{SO}_4$  solutions of different concentrations.

The electrocatalytic activity tests were carried out on pEDOT-pSS/PtRu electrodes by CV at  $5\text{ mV s}^{-1}$  and chronoamperometry (CA) at different electrode potentials in 0.1 M  $\text{H}_2\text{SO}_4$ –0.5 M  $\text{CH}_3\text{OH}$  at room temperature (RT, ca.  $25^\circ\text{C}$ ) and  $60^\circ\text{C}$ . Passive, air-breathing, 1 M  $\text{CH}_3\text{OH}$  solution-fueled DMFCs were built with CP/pEDOT-pSS/PtRu anode and CP/pEDOT-pSS/Pt cathode hot-pressed onto a Nafion<sup>®</sup> 115 membrane (Alfa Aesar), which had been treated in 3%  $\text{H}_2\text{O}_2$ , in water, in 0.5 M  $\text{H}_2\text{SO}_4$  and again in water for 1 h at  $80^\circ\text{C}$  in turn before use. The cells were held together by two transparent acrylic plates to which stainless steel current collectors were fixed. The  $\text{CH}_3\text{OH}$  solution was placed in a reservoir built in the anode plate in contact with the current collector and the back of the CP anode, while oxygen from the surrounding atmosphere diffused into the cathode through the openings of the cathode acrylic plate to air. The air-breathing DMFCs were tested at RT and at  $60^\circ\text{C}$  by LSV at  $5\text{ mV s}^{-1}$  and CA at different cell potentials.

## 2.5. Instrumentation

The pEDOT-pSS were ground with Fritsch Pulverisette 6 planetary ball mill (20 min at 150 rpm and 20 min at 200 rpm). X-ray diffraction analyses of the powders and of the electrodes were performed with a Philips X'Pert diffractometer, a  $\text{Cu K}\alpha$  ( $\lambda = 1.5406\text{ \AA}$ ) radiation source and Ni filter, in continuous mode ( $5\text{--}90^\circ$   $2\theta$  range,  $0.05^\circ$   $2\theta\text{ s}^{-1}$  scan rate) and in step-scanning mode ( $0.04^\circ$   $2\theta$  step,  $1\text{--}10\text{ s step}^{-1}$ ). Scanning electron micrographs were acquired with a Zeiss EVO 50 apparatus equipped with an energy dispersive X-ray analyser (EDS) from Oxford model INCA ENERGY 350 system. The electronic resistivity of pEDOT-pSS was measured via the four-point probe technique using a Jandel Multiheight Probe, an AMEL Model 2053 potentiostat/galvanostat for current supply and a Hewlett Packard 3478A multimeter for voltage reading on plates ( $2\text{ cm}$  diameter) for electronic resistivity measurements obtained by pressing (2 t for 5 min) ca. 0.5 g of pEDOT-pSS. The particle sizes were measured by a Fritsch Analysette 22 Compact laser particle sizer in the  $0.3\text{--}300\text{ }\mu\text{m}$  (62 channel) range with five scans per measurement. All the electrochemical measurements were performed with a potentiostat/galvanostat Voltalab Radiometer Copenhagen PGZ 301 under argon atmosphere in a cell with

separate compartments; the counterelectrode was a Pt coil and the reference electrode was an Ag/AgCl/KCl 0.04 M for PtRu electrodeposition tests and an Hg/Hg<sub>2</sub>SO<sub>4</sub>/K<sub>2</sub>SO<sub>4</sub> for electrocatalytic activity tests (in the following all the potentials are referred to NHE). The tests at 60 °C in 0.1 M H<sub>2</sub>SO<sub>4</sub>–0.5 M CH<sub>3</sub>OH were done in a thermostated cell using a Julabo CC304 thermostat and those in air-breathing DMFC configuration using a thermostatic oven.

### 3. Results and discussion

Repeated CVs of pEDOT-pSS electrodes in 0.1 M H<sub>2</sub>SO<sub>4</sub> between 42 and 842 mV versus NHE were performed and Fig. 1 reports as an example the 450th and 900th CV at 20 mV s<sup>-1</sup> of a D-sample pEDOT-pSS electrode (sprayed on CP<sub>H</sub>) with a polymer loading of ca. 1 mg cm<sup>-2</sup>, a value in the range of those useful for supporting PtRu. The stability of the CV and especially its shape which is fully comparable to that of electrosynthesized pEDOT-pSS, attest that even if the amount of pSS (EDOT:SS = 1:1 in D samples) is increased with respect to that involved in electrosynthesized pEDOT-pSS, the electronic and ionic transport properties of the polymer composites are still good. Given that the CV voltage excursion covers the potentials both for anodic oxidation of methanol and for cathodic reduction of oxygen, the viability of pEDOT-pSS composites as supports for both PtRu and Pt catalysts in DMFCs is evident. The excess of pSS assures good ionic conductivity, a fact of paramount importance for the use of pEDOT-pSS without Nafion<sup>®</sup> added in the electrodes because pSS is a proton or, more generally, a cation exchanger.

Electronic resistivity measurements of samples D and E were performed both on hand-ground and on ball-milled powders: the latter showed better conductivity values than the former, thus indicating that the electronic resistivity greatly depends on the grain boundaries in the pressed plates. The ball-milled D sample displayed a higher electronic conductivity (11 S cm<sup>-1</sup>) than that of E sample (0.04 S cm<sup>-1</sup>), which may be ascribed to the lesser amount of pSS in the composite of the former. Laser analysis determined particle (or aggregate) size: 50% of the particles had <70 μm diameter in the hand-ground samples and <35–40 μm

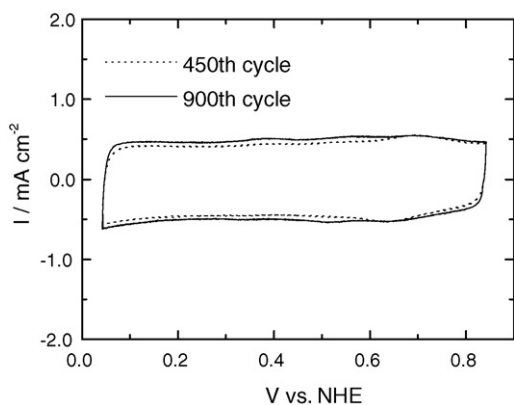


Fig. 1. 450th and 900th CVs at 20 mV s<sup>-1</sup> at RT in H<sub>2</sub>SO<sub>4</sub> 0.1 M of chemically prepared D CP<sub>H</sub>/pEDOT-pSS (1.1 mg cm<sup>-2</sup>); charge = 20 mC cm<sup>-2</sup>, coulombic efficiency = 99.9%.

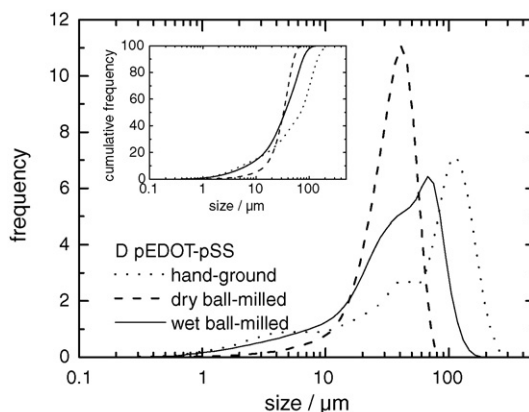


Fig. 2. Particle size frequency (%) of differently ground D pEDOT-pSS. The inset shows the cumulative frequency (%) of particle size.

in the dry and wet (i.e. in presence of small amount of water) ball-milled samples. The particle distributions in Fig. 2 show the difference among the differently ground samples. While the diversity between dry and wet-ground samples only slightly affected the resistivity data, it significantly reflects on the properties and homogeneity of the 2-propanol suspensions of these powders (the wet-ground being the best) in preparing electrodes by spray deposition.

The intrinsic ionic conductivity of the D and E samples was evaluated at RT from impedance measurements in H<sub>2</sub>SO<sub>4</sub> solutions of different concentrations by plotting the pEDOT-pSS ionic conductivity versus the electrolyte conductivity as reported in Fig. 3 for sample D. The pEDOT-pSS ionic conductivity values were calculated after [23,25] using the resistance resulting from the subtraction of the electrolyte resistance ( $R_E$ ) from the value of the resistance ( $R_2$ ) intercepted by the limit capacitance (see the inset in Fig. 3) according to the formula

$$\sigma = \frac{\tau}{3A(R_2 - R_E)}$$

where  $\tau$  is the thickness and  $A$  is the area of the electrode. The intrinsic ionic conductivity of pEDOT-pSS as calculated by the intercept of the straight line (see Fig. 3), ca. 0.02 mS cm<sup>-1</sup> for

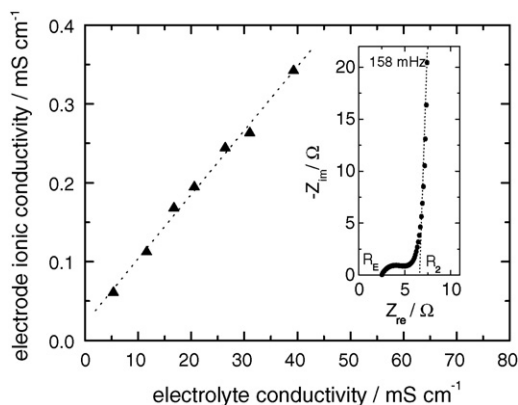


Fig. 3. Ionic conductivity values of CP<sub>5</sub>/D pEDOT-pSS from impedance measurements at RT vs. electrolyte conductivity. The inset shows the impedance plot at +442 mV vs. NHE between 100 kHz and 158 mHz in 0.1 M H<sub>2</sub>SO<sub>4</sub>.

sample D and  $0.01 \text{ mS cm}^{-1}$  for sample E, is lower than that reported in literature (ca.  $0.5 \text{ mS cm}^{-1}$ ) [23]. Despite the lower intrinsic conductivity values found for our pEDOT-pSS samples, the electrocatalytic tests in passive DMFC configuration confirmed that the proton transport properties of the pEDOT-pSS we prepared were significant (vide infra).

We prepared electrodes for PtRu electrochemical deposition with both samples D and E, whereas for PtRu and Pt chemical deposition we used, on the basis of the higher electronic conductivity, only sample D. We carried out XRD, SEM and EDS analyses of pEDOT-pSS powders and electrodes on which noble metals were deposited chemically or electrochemically. Fig. 4a shows the XRD spectra of D pEDOT-pSS/PtRu, of D pEDOT-pSS/Pt and of bare pEDOT-pSS powders. The cell parameter, both from Lorentzian fitting on the 220 peak and from a total fitting on the 111, 220 and 311 peaks, was  $3.908 \text{ \AA}$  for PtRu and  $3.917 \text{ \AA}$  for Pt, in accord with the decreasing of the cell parameter when the PtRu alloy is formed. The crystallite size was evaluated using the Scherrer equation for the 220 peak and was  $5.2 \text{ nm}$  and  $2.8 \text{ nm}$  for PtRu and Pt, respectively. Electrochemically deposited PtRu on D and E samples elicited XRD spectra similar to that reported in Fig. 4a even if, due to the lower amount (ca. 2 order of magnitude) of the catalyst in the analyzed sample, the intensity of the peak dramatically decreased so that the cell

parameters were estimated by the most intense 111 peak analysis and were  $3.889$  and  $3.893 \text{ \AA}$ , with crystallite sizes of  $5.0$  and  $4.9 \text{ nm}$  for samples D and E, respectively.

SEM analysis of D pEDOT-pSS/PtRu and of D pEDOT-pSS/Pt powders and electrodes evinced the presence of large metal aggregates made of smaller particles ( $600\text{--}150 \text{ nm}$ ). The backscattered SEM image of D pEDOT-pSS/PtRu powder in Fig. 4b is an example.

EDS analysis confirmed the presence of Ru for all the pEDOT-pSS/PtRu samples. The Pt:Ru ratio in the metal catalyst is not homogeneous all over the sample and in some cases differs from the 1:1 ratio of the precursors in the chemical or electrochemical deposition bath; Pt:Ru atomic ratio of 47:53 was estimated for the sample in Fig. 4a.

The tests of electrocatalytic activity for methanol oxidation were performed in  $0.1 \text{ M H}_2\text{SO}_4\text{--}0.5 \text{ M CH}_3\text{OH}$  at RT and  $60^\circ\text{C}$  on CP<sub>S</sub>/D pEDOT-pSS/PtRu and CP<sub>S</sub>/E pEDOT-pSS/PtRu (samples D and E, with electrodeposited PtRu) electrodes and on CP<sub>S</sub>/D pEDOT-pSS/PtRu (with chemical deposited PtRu) electrodes. The specific catalytic activity was evaluated by referring to the amount of Pt in the catalyst, an amount that was experimentally estimated after mineralization of all the electrodes by the colorimetric method reported in Section 2. Fig. 5a shows, as an example, the CV at  $5 \text{ mV s}^{-1}$  between  $42$  and  $642 \text{ mV}$  versus NHE at  $60^\circ\text{C}$  of CP<sub>S</sub>/E pEDOT-pSS with PtRu electrochemical deposited (curve 1). Before PtRu electrochemical deposition, the CP<sub>S</sub>/E pEDOT-pSS support was tested in the same conditions to better evaluate the onset potential of the methanol oxidation

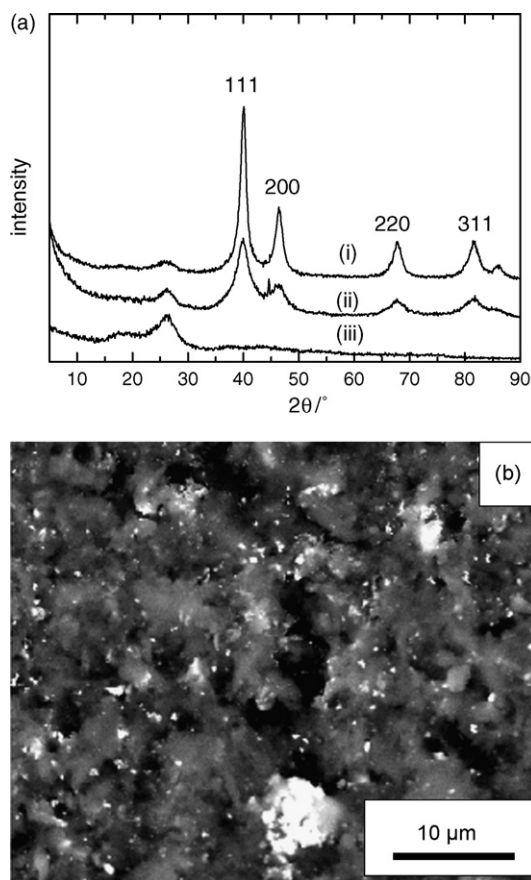


Fig. 4. (a) XRD spectra of (i) D pEDOT-pSS/PtRu, (ii) D pEDOT-pSS/Pt and (iii) bare pEDOT-pSS powders; (b) SEM image of D pEDOT-pSS/PtRu (chemical PtRu, Pt content = 17% of the total composite).

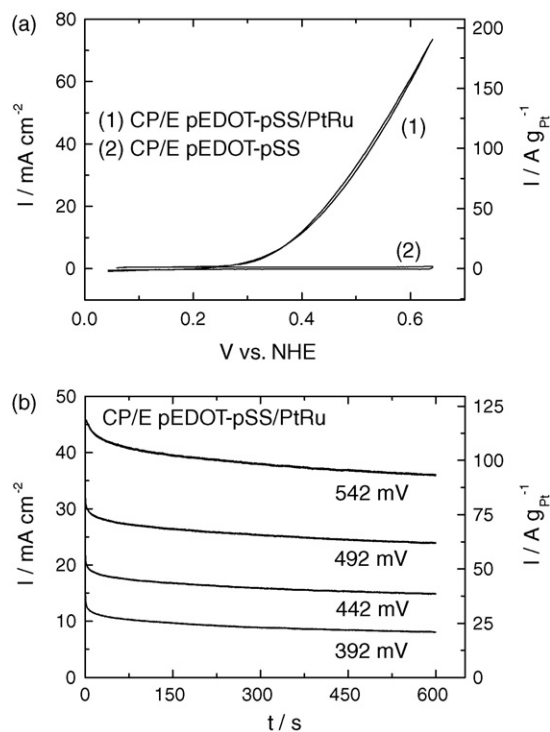


Fig. 5. Electrocatalytic activity of CP<sub>S</sub>/E pEDOT-pSS/PtRu ( $2.27 \text{ mg cm}^{-2}$ , electrochemical PtRu, Pt =  $0.39 \text{ mg cm}^{-2}$ ) in  $0.1 \text{ M H}_2\text{SO}_4\text{--}0.5 \text{ M CH}_3\text{OH}$  at  $60^\circ\text{C}$ : (a) CV of the electrocatalytic electrode and of the bare support at  $5 \text{ mV s}^{-1}$  between  $42$  and  $642 \text{ mV}$  vs. NHE; (b) CA curves at different potentials ( $542$ ,  $492$ ,  $442$ ,  $392 \text{ mV}$  vs. NHE).



Table 1  
Electrocatalytic activity of different CP/pEDOT-pSS/PtRu electrodes from CA at 492 mV vs. NHE in 0.1 M H<sub>2</sub>SO<sub>4</sub>–0.5 M CH<sub>3</sub>OH at 60 °C

Support	PtRu catalyst	Pt (wt%)	Pt (mg cm <sup>-2</sup> )	<i>I</i> <sub>492 mV,600 s</sub> (A g <sub>Pt</sub> <sup>-1</sup> )
Chemical D pEDOT-pSS	Chemical	17	0.2–0.3	19 ± 2
	Electrochemical	16	0.1–0.6	50 ± 11
Chemical E pEDOT-pSS	Electrochemical	16	0.2–0.6	52 ± 9

process and the CV at 60 ° of the polymer support is also reported (curve 2). The onset potentials for samples E and D were in the range 0.24–0.27 V versus NHE, values which are lower than expected for Pt alone and confirm the presence of Ru in the catalyst. Fig. 5a shows that the catalytic current at 60 °C was 80 A g<sub>Pt</sub><sup>-1</sup> at 492 mV, a very interesting value; from CV at RT (not shown in the figure) the catalytic current was measured as 8 A g<sub>Pt</sub><sup>-1</sup>, i.e. one-tenth of the value at 60 °C. Fig. 5b shows the CA at 60 °C and at potentials from 392 to 542 mV versus NHE of the same electrode and the specific catalytic current at 492 mV went from 71 A g<sub>Pt</sub><sup>-1</sup> after 1 min to 62 A g<sub>Pt</sub><sup>-1</sup> after 10 min, values that compare well with that from CV. Some preliminary stability tests at 60 °C and 492 mV showed that after 7 h the current was still 50% of that recorded after 10 min.

Table 1 displays the specific catalytic currents for methanol oxidation after 600 s from CA at 492 mV versus NHE in 0.1 M H<sub>2</sub>SO<sub>4</sub>–0.5 M CH<sub>3</sub>OH at 60 °C for PtRu chemically and electrochemically deposited on pEDOT-pSS. The data were averaged over the values of 5–10 electrodes with PtRu loading such that the Pt content ranged from 0.2 to 0.3 mg cm<sup>-2</sup> for the D pEDOT-pSS electrodes with chemical PtRu, from 0.1 to 0.6 mg cm<sup>-2</sup> for the D pEDOT-pSS with electrochemical PtRu and from 0.2 to 0.6 mg cm<sup>-2</sup> for the E pEDOT-pSS with electrochemical PtRu. The results in Table 1 show that the specific catalytic activities of PtRu electrochemically deposited on the two polymer supports from samples D and E are almost equivalent. Indeed, being at 492 mV ca. 50 A g<sub>Pt</sub><sup>-1</sup>, they are notably near to those found for PtRu supported on carbons of optimized mesoporosity developed in our laboratory, which in turn were double the catalytic activity found for PtRu supported on Vulcan commercial carbon [26].

The lower performance of the electrocatalyst chemically deposited onto pEDOT-pSS is presumably due to the Teflon<sup>®</sup> that was added in order to obtain a composite suitable for spreading onto CP current collectors. However, Teflon<sup>®</sup> can insulate metal particles and thus decrease the electrocatalytic activity.

Given that the catalytic activity reported in Table 1, particularly for electrodeposited PtRu, may take advantage of the proton conductivity of the H<sub>2</sub>SO<sub>4</sub>–CH<sub>3</sub>OH liquid phase, we performed tests by configuring passive DMFC assembled with electrodes based on D pEDOT-pSS/PtRu and D pEDOT-pSS/Pt (with pEDOT-pSS, PtRu and Pt chemically prepared). The electrodes were made by spraying isopropyl alcohol-based inks of the D pEDOT-pSS/PtRu and D pEDOT-pSS/Pt powders, without Teflon<sup>®</sup> or Nafion<sup>®</sup>, on CP; they were then dried and weighed to evaluate Pt content in the two catalyst layers. Fig. 6a shows the LSVs at 5 mV s<sup>-1</sup> between the open circuit and the short circuit voltages at 60 °C, and Fig. 6b reports CAs at the same

temperature and at selected cell potentials of a passive DMFC based on pEDOT-pSS/PtRu (17 wt% Pt, 0.18 mg<sub>Pt</sub> cm<sup>-2</sup>) and pEDOT-pSS/Pt (22 wt% Pt, 0.10 mg<sub>Pt</sub> cm<sup>-2</sup>). It is evident from the figures that the current values from CAs and LSVs are almost the same.

Given that there are very few studies on pEDOT-pSS or on other polymers in DMFC configuration and none in passive DMFC, we also assembled and tested for comparison DMFCs in which both anode and cathode were Vulcan XC-72R commercial carbon on which we chemically deposited PtRu (16 wt% Pt, 0.27 mg<sub>Pt</sub> cm<sup>-2</sup>) and Pt (30 wt% Pt, 1.6 mg<sub>Pt</sub> cm<sup>-2</sup>). In addition, as the passive DMFC based on pEDOT-pSS was cathode-limited, i.e. the amount of Pt on the cathode was even lower than that in the PtRu catalyst on anode, we also assembled a cell with a pEDOT-pSS/PtRu anode (27 wt% Pt, 0.31 mg<sub>Pt</sub> cm<sup>-2</sup>) and a Vulcan/Pt cathode (30 wt% Pt, 2.03 mg<sub>Pt</sub> cm<sup>-2</sup>). The type and Pt content of the electrodes used in the tested passive DMFCs and the ratio (*R*<sub>±</sub>) of the Pt content of the cathode catalyst to the

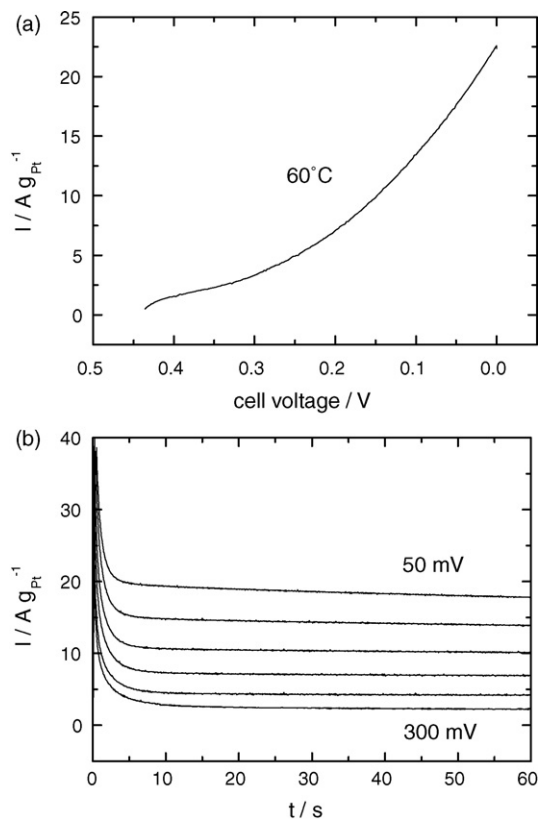


Fig. 6. Passive DMFC CPs/D pEDOT-pSS/PtRu (0.18 mg<sub>Pt</sub> cm<sup>-2</sup>)/Nafion<sup>®</sup> 115/Pt (0.1 mg<sub>Pt</sub> cm<sup>-2</sup>)/pEDOT-pSS/CPs. (a) LSVs at 5 mV s<sup>-1</sup> at 60 °C; (b) CAs at cell potentials of 300, 250, 200, 150, 100 and 50 mV at 60 °C.

Table 2  
Catalytic activity of passive DMFCs at 60 °C with 1 M CH<sub>3</sub>OH solution

Anode type and Pt loading in PtRu	Cathode type and Pt loading	$R_{\pm}$	$I_{\max}$ (A g <sub>anode Pt</sub> <sup>-1</sup> )	$P_{\max}$ (W g <sub>anode Pt</sub> <sup>-1</sup> )
D pEDOT-pSS/PtRu, Pt = 17 wt%, 0.18 mg cm <sup>-2</sup>	D pEDOT-pSS/Pt, Pt = 22 wt%, 0.10 mg cm <sup>-2</sup>	0.6	10	1.5
D pEDOT-pSS/PtRu, Pt = 27 wt%, 0.31 mg cm <sup>-2</sup>	Vulcan/Pt, Pt = 30 wt%, 2.03 mg cm <sup>-2</sup>	6.6	12	2.2
Vulcan/PtRu, Pt = 16 wt%, 0.28 mg cm <sup>-2</sup>	Vulcan/Pt, Pt = 30 wt%, 1.28 mg cm <sup>-2</sup>	4.6	11	2.2
DEMO/PtRu, Pt ≥ 3.7 mg cm <sup>-2</sup>	DEMO/Pt, Pt ≥ 6.6 mg cm <sup>-2</sup>	1.8	7	2.0

anode catalyst are reported in Table 2, which also summarizes the catalytic activity results of these passive DMFCs compared with those of a commercial (demonstrative) passive DMFC with the same assembly and with electrodes denoted by DEMO.

The catalytic activity data in Table 2, i.e. the maximum specific catalytic current and the maximum specific power, were obtained by plots like those reported in Fig. 7 for the air-breathing cells with the catalysts PtRu and Pt both supported on pEDOT-pSS (Fig. 7a) and for the cell with the PtRu supported on pEDOT-pSS and Pt on Vulcan carbon (Fig. 7b). The cell potential and specific power versus specific catalytic current plots were built from the results of 60 s-CA tests at RT and 60 °C in which the Pt content only in the PtRu anode catalyst and the electrode area actually in contact with the methanol reservoir (3 cm<sup>2</sup>) were taken into account.

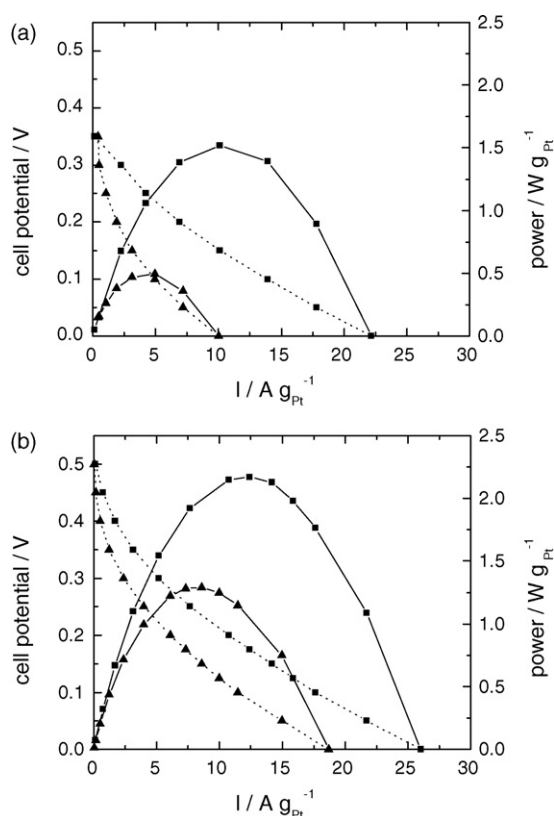


Fig. 7. Plots of cell voltage (dotted lines) and specific power (solid lines) vs. specific catalytic current of passive DMFCs at RT (triangles) and 60 °C (squares): (a) CPs/D pEDOT-pSS/PtRu (0.18 mg<sub>Pt</sub> cm<sup>-2</sup>)/Nafion<sup>®</sup> 115/Pt (0.10 mg<sub>Pt</sub> cm<sup>-2</sup>)/pEDOT-pSS/CPs and (b) CPs/D pEDOT-pSS/PtRu (0.31 mg<sub>Pt</sub> cm<sup>-2</sup>)/Nafion<sup>®</sup> 115/Pt (2.03 mg<sub>Pt</sub> cm<sup>-2</sup>)/Vulcan/CP<sub>H</sub>.

The Pt content in the PtRu catalyst of the anodes tested in passive DMFCs was of the same order of magnitude, for a better comparison, as that of the electrodes tested in liquid solution, with the exception that the Pt content in the demonstrative DMFC was more than one order of magnitude higher. Though high values of catalytic current or power per cm<sup>2</sup> could not be expected with a Pt loading of 0.1–0.3 mg cm<sup>-2</sup>, the specific catalytic current and specific power values are worth noting. The specific maximum power at 60° of the passive DMFC with both electrode catalysts supported on D pEDOT-pSS was 1.5 W g<sub>Pt</sub><sup>-1</sup>, with current of 10 A g<sub>Pt</sub><sup>-1</sup>, values comparable to those of the passive DMFC with Vulcan/PtRu and of the passive demo DMFC even if the cell worked in cathode-limited condition. This means that pEDOT-pSS is a good protonic conductor, as we wanted to demonstrate, and that our cell assembly and that of the demonstrative cell are almost equivalent. Better results, as expected, were obtained for the pEDOT-pSS/PtRu anode coupled with a cathode containing a greater amount of Pt, which reached a specific maximum power of 2.2 W g<sub>Pt</sub><sup>-1</sup> with current of 12 A g<sub>Pt</sub><sup>-1</sup>. It is also worth noting that all the tested carbon-based electrodes contained ca. 20 wt% Nafion<sup>®</sup> and the pEDOT-pSS-based electrodes were Nafion<sup>®</sup>-free, which is a further confirmation of the good protonic transport in pEDOT-pSS composites. Experiments on passive DMFCs with higher PtRu loading on pEDOT-pSS and without cathode-catalyst limitation, with particular focus on the electrocatalytic performance stability are in progress and will be reported elsewhere.

#### 4. Conclusions

The results of the catalytic activity tests of Nafion<sup>®</sup>-free pEDOT-pSS/PtRu electrodes in aqueous 0.1 M H<sub>2</sub>SO<sub>4</sub>–0.5 M CH<sub>3</sub>OH solution were confirmed by their performance in passive DMFC configuration with Nafion<sup>®</sup> 115 membrane and pEDOT-pSS/Pt or Vulcan/Pt cathode electrodes. DMFC performance with the catalysts supported on Nafion<sup>®</sup>-free pEDOT-pSS compares well with that of the passive DMFCs we assembled with both the catalysts on Vulcan carbon supports containing 20 wt% Nafion<sup>®</sup>, thereby confirming the good protonic transport inside our pEDOT-pSS.

To our knowledge this is the first time that data for DMFCs with the anode or both electrode catalysts supported on pEDOT-pSS are reported. These promising results are of particular importance given that a growing concern is the stability of carbon catalyst supports against corrosion, a phenomenon that should not affect pEDOT-pSS because it is well recognized as a stable conducting polymer.

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