

Methanol oxidation by pEDOT-pSS/PtRu in DMFC

Catia Arbizzani, Maurizio Bisio, Elisa Manferrari, Marina Mastragostino*

University of Bologna, Department of Metal Science, Electrochemistry and Chemical Techniques, via San Donato 15, 40127 Bologna, Italy

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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 H₂SO₄–0.5 M CH₃OH liquid solution and in passive, air-breathing DMFC configuration with Nafion[®] 115 protonic membrane and 1 M CH₃OH are reported and discussed.

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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 H₂SO₄–0.5 M CH₃OH liquid solution as well as of tests in passive, air-breathing DMFC configuration with Nafion[®] 115 membrane and 1 M CH₃OH 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

* Corresponding author. Tel.: +39 0512099798; fax: +39 0512099365.

E-mail address: marina.mastragostino@unibo.it (M. Mastragostino).

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°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 H_2PtCl_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_S and Hydro2Power, Italy, 0.3 mm thick, CP_H). For the first type, an aqueous slurry containing 85–80 wt% pEDOT-pSS and 15–20 wt% Teflon[®] (Dupont, 60% aqueous emulsion) was spread onto CP in which Kapton[®] (Dupont) adhesive tape was used to delimit a 1 cm^2 area. These electrodes had pEDOT-pSS loadings from 0.5 to 4 mg cm^{-2} and were used as support for electrochemical deposition of PtRu. For the second type, a 10 wt% Teflon[®] (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 cm^2 delimited area to reach pEDOT-pSS/PtRu loadings from 0.85 to 1.6 mg cm^{-2} . For the third, a 2-propanol-based ink (without Nafion[®] added) of pEDOT-pSS was sprayed onto 1 cm^2 CP electrodes; the pEDOT-pSS loadings were ca. 1 mg cm^{-2} . For the fourth type, two 2-propanol-based inks (without Nafion[®]) of pEDOT-pSS/PtRu and of pEDOT-pSS/Pt were sprayed onto 4 cm^2 CP electrodes for DMFC assembly. A small amount of a 1 wt% of Nafion[®] solution in water was sprayed on top of the electrodes just before hot pressing them onto Nafion[®] 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 mV s^{-1} in 0.1 M H_2SO_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 H_2SO_4 solutions of different concentrations.

The electrocatalytic activity tests were carried out on pEDOT-pSS/PtRu electrodes by CV at 5 mV s^{-1} and chronoamperometry (CA) at different electrode potentials in 0.1 M H_2SO_4 –0.5 M CH_3OH at room temperature (RT, ca. 25°C) and 60°C . Passive, air-breathing, 1 M CH_3OH solution-fueled DMFCs were built with CP/pEDOT-pSS/PtRu anode and CP/pEDOT-pSS/Pt cathode hot-pressed onto a Nafion[®] 115 membrane (Alfa Aesar), which had been treated in 3% H_2O_2 , in water, in 0.5 M H_2SO_4 and again in water for 1 h at 80°C in turn before use. The cells were held together by two transparent acrylic plates to which stainless steel current collectors were fixed. The CH_3OH 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°C by LSV at 5 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 ($5\text{--}90^\circ$ 2θ range, 0.05° $2\theta\text{ s}^{-1}$ scan rate) and in step-scanning mode (0.04° 2θ 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 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

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