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Electrosynthesis of Co/PPy nanocomposites for ORR electrocatalysis: a study based on quasi-in situ X-ray absorption, fluorescence and in situ Raman spectroscopy

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ABSTRACT

Cobalt/polypyrrole ORR electrocatalysts has been electrochemically synthesized by a potentiostatic anodic/cathodic pulse-plating procedure. The deposition electrochemistry has been studied by cyclic voltammetry and in-situ Micro Raman Spectroscopy complemented with scanning X-ray microscopy and micro-spot X-ray absorption spectroscopy (μ-XAS). Linear sweep voltammetry (LSV) under oxygen reduction has been used to assess the electrocatalytic effect of as-electrodeposited Co/PPy. The obtained results have provided new information about the concomitant electropolymerisation and metal incorporation processes occurring under different pulsed co-electrodeposition conditions, important for optimising the electrosynthesis procedure. The colocation of O and Co, evidenced by the O and Co XRF maps indicates that the Co in the formed composite is in oxidized state and for composites formed at low currents using shorter Co pulses coexistence of both CoO and Co_3O_4 is evidenced by the Co L_3 XAS spectra. Bimodal Co distribution as micro-grains on a background of nano-grains and co-nulcleation of PPy and Co is evidenced by correlation of Co and N XRF maps.

1. Introduction

Since the first demonstration of the catalytic activity of cobalt phthalocyanine and other transition metal macrocycles in oxygen reduction reaction (ORR) [1], the non-precious metal-nitrogen-carbon (M/N/C) catalysts have been extensively studied as possible substitutes of the expensive Pt-based air cathodes. Promising properties have been reported for the novel ORR active Me/N_x/C moieties synthesized employing a multiplicity of metal, nitrogen and carbon precursor materials [2–9]. Among them, the conjugated heterocyclic conducting polymers have been suggested as low-cost nitrogen sources for the fabrication of highly active M-N-C ORR electrocatalysts [10–17]. The high electrical conductivity [18] and easy synthesis via chemical [19] or electrochemical [20] routes of Polypyrrole (PPy), makes it very promising as a catalyst support [21] for metal oxides [22] and metal-based complexes [23,24].

To date, the most common procedures to prepare Co/PPy electrocatalysts involve functionalization of carbon nanoparticles by chemical polymerization of pyrrole followed by the chemical reduction or impregnation of a cobalt salt into the polymer [15,25–27]. Another promising procedure is electropolymerization in a fluid-bed cell [28], leading to the formation of a cobalt-modified PPy film supported on carbon nanoparticles. Carbon-particle supported Co/PPy electrocatalysts are typically incorporated into a suitable ink and deposited onto the electrode surface by conventional spraying or printing processes. A convenient alternative method is the direct electrodeposition of Co/PPy/C catalysts, using anodic polarization to electropolymerize pyrrole as a film and cathodic polarization to deposit the metal into the polymer structure. Electrochemistry also allows the fine-tuning of the morphological and chemical properties of the catalyst by the simple control of electrical parameters. The co-electrodeposition of PPy and metal nanoparticles is possible for Au [29], Ni [30] and Fe [31] starting from solutions containing pyrrole and a metal salt. A few papers deal with ORR studies of Co/PPy electrocatalysts prepared by electrosynthesis [32,33].

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In the present paper we combine Raman spectroscopy with X-ray imaging and microspectroscopy methods to shed light on the morphology and composition of Co/PPy electrocatalysts, synthesized via the electrochemical route proposed in [33].

2. Experimental

2.1. Materials and Electrodes

Acetonitrile, $CoCl_2 \cdot 6H_2O$ and pyrrole were supplied by Aldrich. Before each electrodeposition pyrrole monomer was distilled under rotary pump vacuum several times (typically 2-3) until it became colorless. All the solutions were prepared with ultrapure water with a resistivity of 18.2 MΩ·cm. The electrochemical syntheses were performed using a classic three-electrode cell with a glassy carbon rod ($\Phi = 3$ mm), graphite disk ($\Phi = 10$ mm) and gold rod ($\Phi = 5$ mm) as working electrodes (WE), a Pt wire spiral (2 cm^2 for Raman measurements, 5 cm^2 for the other experiments) as counter electrode (CE) and an aqueous silver/silver chloride (Ag/AgCl/3 M: 0.209 V/NHE) as reference electrode (RE), connected to the solution by a salt bridge. The liquid junction potential between aqueous and non-aqueous solution has been checked to be negligible. All the potentials are referred to the Ag/AgCl/3 M scale.

2.2. Electrochemical measurements and methods

The electrochemical measurements were performed at room temperature using ParStat and VersaStat potentiostats. Cyclic voltammetric analyses have been carried out at glassy carbon electrodes in the range - 1.2 - 1.2 V at a scan rate of 100 mVs^{-1} in de-aerated acetonitrile solutions containing 1% v/v H_2O and 0.1 M TBAP (tetrabutyl-ammonium-perchlorate) supporting electrolyte, with additions of: (i) 0.1 M pyrrole; (ii) 0.05 M $CoCl_2$ and (iii) both 0.1 M pyrrole and 0.05 M $CoCl_2$. N_2 (Rivoira, 5 N) was bubbled for 20 min into the solution before the measurement and an N_2 blanket was kept above the solution during electrochemistry. The WEs were polished mechanically to a mirror finish before each experiment and subsequently subjected to ultra-sonication in distilled water for 10 min and electrochemical oxidation of impurities in 0.5 M H_2SO_4 from 0 to 1.5 V at a scan rate of 100 mVs^{-1}, as recommended in [33]. The counter electrode was cleaned by immersion in concentrated HNO_3 to remove the metal and by annealing in a butane flame to eliminate organic residues.

The Co/PPy catalysts have been synthesized on graphite disks or glassy carbon (GC) electrode by electrodeposition in de-aerated acetonitrile solutions containing 0.1 M pyrrole, 0.05 M $CoCl_2$ 1% v/v H_2O and 0.1 M TBAP supporting electrolyte according to a step pulsed potential procedure elaborated on that recently suggested in the literature [33]. It consists in the repetition of an optimized cycle composed by an initial step at 0 V for 1 s to relax the compositional double layer, a subsequent anodic pulse at 1.2 V for 0.5 s to electrodeposit PPy, a cathodic step at -1.8 V for 0.5 s to incorporate into PPy reduced Co species and a final anodic step at 1.2 V for 0.2 s to deposit another layer of PPy. The potential values have been selected according to the cyclic voltammetric results reported in [33] and in this work.

The electrocatalytic activity of Co/PPy electrodeposited on GC (60 cycles of pulsed deposition) towards ORR was evaluated by linear sweep voltammetric (LSV) measurements in O_2-saturated (SIAD 6.0) 0.1 M KOH electrolyte at different potential scan rates. For reference purposes, the same electrochemical experiments were duplicated with solutions that had been de-oxygenated by N_2 saturation. O_2 was bubbled for 20 min into the solution before the measurements and an O_2 blanket was maintained above the electrolyte during voltammetry. The current density values used to determinate the ORR Tafel and Randles-Sevcik slopes have been depurated by the N_2-background. Current densities are given in terms of geometric area. All the potentials reported in the text and in the graphs are referred to the Ag/AgCl/3 M scale. For comparison purposes the literature potentials referred to RHE electrode have been converted to Ag/AgCl scale with the transformation: $E_{AgAgCl} = E_{RHE}$-0.976.

2.3. In situ Raman spectroscopy

Raman spectra were recorded using a LabRam microprobe confocal system. A 50× long-working distance objective was used and the excitation line at 632.8 nm was provided by a 12 mW He-Ne laser. The slit and pinhole were set at 200 and 400 μm, respectively, corresponding to a scattering volume of ~3 pL; Raman spectra were acquired with a 600 grid/mm spectrometer. The recorded Raman intensities are directly proportional to the discharge current of the CCD detector. In situ electrochemical measurements were performed in Ventacon® glass cells with a gold disc electrode embedded in a Teflon holder. The counter electrode was a Pt wire loop concentric and coplanar with the working electrode. In order to achieve SERS activity the gold electrode was submitted to ORC treatment consisting in cycling the electrode in a separated cell in 0.1 M KCl from 0.3 V to 1.2 V at 500 mVs^{-1} for 50 times. Further details on the electrodes preparation and electrochemical procedures are indicated in Sections 2.1 and 2.2.

2.4. Soft X-ray absorption and fluorescence mapping

Soft X-ray transmission microscopy (STXM) experiments, combined with X-ray fluorescence (XRF) elemental mapping and micro-spot X-ray absorption spectroscopy (XAS) were performed at the TwinMic beamline of Elettra synchrotron facility (Trieste, Italy) [34,35]. The photon beam was focused to a microprobe using zone plate optics and the imaging measurements were performed by simultaneous detection of transmitted and emitted (fluorescence) photons raster-scanning the sample with respect to the microprobe. The transmitted photons were detected using a fast readout CCD camera, generating absorption and phase contrast images [36,37], whereas the emitted fluorescence signal was collected by means of 8 Silicon Drift Detectors located in an annular geometry in front of the specimen [38,39]. The XAS spectra acquired from specific points of interest selected from the X-ray absorption images and the XRF maps were measured using a photodiode located downstream the specimen.

3. Results and discussion

3.1. Electrodeposition of Co/PPy composites

3.1.1. Cyclic voltammetry

3.1.1.1. Electropolymerization of pyrrole. The electropolymerization of pyrrole in 0.1 M TBAP and 1% v/v H_2O de-areated acetonitrile (ACN) solution was followed by cyclic voltammetry in the range -1.2-1.2 V, as reported in Fig. 1. As frequently observed in the literature regarding conducting polymers [40], the first cycle (Fig. 1-a) shows a typical “nucleation loop” [41]. During the first anodic scan the electropolymerization of pyrrole appears at ~ 0.85 V on fresh glassy carbon surface and the CV exhibits a crossing on the cathodic-going scan at ~ 0.8 V. The subsequent CV cycles (Fig. 1, Panels (a) and (b)) follow the classical PPy electropolymerization behavior observed in the literature in similar conditions: (i) on the anodic-going scan, an oxidation wave (I) at ~0.4 V followed by a large plateau and a rapid increase of current-density (c.d.) and (ii) on the cathodic-going scan, a reduction wave (II) at ~0 V. These