



# Morphochemical evolution during ageing of pyrolysed Mn/polypyrrole nanocomposite oxygen reduction electrocatalysts: A study based on quasi-in situ photoelectron spectromicroscopy



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## ABSTRACT

This study deals with the morphological and chemical-state changes caused by the degradation of nanocomposite electrocatalysts – fabricated by pulsed potentiostatic co-electrodeposition and subsequently pyrolysed – under oxygen reduction reaction (ORR) conditions in aqueous alkaline solution. Variations in shape, dimensions and chemical state of the Mn-centres were followed by quasi-in situ synchrotron-based scanning photoelectron microscopy with submicron lateral resolution, combined with ex situ Raman measurements, in correspondence of different cyclic voltammetric ageing stages. The decline of the electrocatalytic performance is accompanied by size variations of the MnO<sub>x</sub> particles that are initially ~ 30 nm in diameter, then shrink to ~ 10 nm and subsequently grow to ~ 45 nm after prolonged ORR. Concerning chemical state, the pristine Mn<sup>0,II</sup> nanoparticles are converted to Mn<sup>III,IV</sup> oxy-hydroxides as a result of a dissolution/redeposition process favoured by the oxygen environment.

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## 1. Introduction

The oxygen reduction reaction (ORR) in alkaline solutions is an important issue in both alkaline fuel cells [1] and metal/air batteries [2], and great efforts have been devoted to the replacement of expensive platinum with novel low-cost electrocatalysts. Among the non-noble metal catalysts that have been considered [3,4], carbon-supported transition metal/nitrogen/carbon-based (M/N/C, M = Co, Fe, Mn, etc.) materials have been the object of intense research efforts. The M/N/C pioneering materials were metal porphyrins (MPs) [5], that exhibited sound ORR activity, but serious instability under operating condition [6]. After the discovery that pyrolysis at high temperatures (400–800 °C) notably increases the stability as well as the catalytic activity of MPs (and, more generally, of N<sub>4</sub>-macrocycles), a variety of pyrolysed MP complexes have been studied as possible catalysts for cathodic ORR [7–14]. The mechanism underlying the modifications of the active sites during pyrolysis is still under debate; however the better substantiated hypothesis indicates the formation of MeN<sub>x</sub>-type moieties as responsible of the increased electrocatalytic activity [7,15–18]. Subsequently, several papers have appeared on the fabrication of ORR active materials by pyrolysis of metal and nitrogen/carbon precursors of

different chemical nature with respect to MPs [19–26]. Polypyrrole, as well as other conjugated polymers, has gained great attention as N-source for these processes because of its relatively high nitrogen content, environmental stability, high electrical conductivity [27], excellent ability to support catalysts such as metal oxides [28] and complexes [29, 30] as well as its ease of synthesis by chemical [31] or electrochemical [32] routes. Regarding the metal centre, manganese oxides are probably the most widely used cathode in metal/air batteries, owing to its lower cost, high catalytic activity for oxygen electroreduction in alkaline solution and capability to decompose hydrogen peroxide [33–35]. It is well known that the ORR involves two competitive pathways: the complete 4-electron and the 2-electron reduction mechanisms, producing highly oxidising H<sub>2</sub>O<sub>2</sub>. MnO<sub>x</sub> possesses high catalytic activity towards the purely chemical disproportionation reaction of HO<sub>2</sub><sup>-</sup> in alkaline solution, driving the ORR towards the complete four electron pathway [34,35]. While an extensive literature corpus details the ORR mechanism at cobalt and iron species embedded, in various forms, into polypyrrole, just a few papers have dealt with composite Mn/PPy electrocatalysts [36].

As far as the fabrication of metal/PPy electrocatalytic composites is concerned, at present the most common protocols involve the functionalisation of carbon nanoparticles by the chemical polymerisation of pyrrole followed by the chemical reduction of a metal salt, impregnated into the polymer [37–40]. This process is typically followed by pyrolysis,

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which drastically increases both catalytic activity [36,37] and durability [41,42] of polypyrrole–metal compounds. Electrodeposition is a convenient one-pot route to functionalise carbon substrates with M/N/C catalysts; moreover, provided that an adequate level of fundamental mechanistic understanding is available, electrochemical growth gives the opportunity to gain fine control over the morphological and chemical properties of the electrodeposits, resulting in potential control on activity, selectivity and durability of the catalyst [43]. Starting from a solution containing pyrrole and a metal salt, the co-electrodeposition of PPy and metal nanoparticles has been proved to be possible for gold [44], nickel [45] and iron [46]. Galvanostatic anodic electrodeposition of MnO<sub>2</sub> into PPy has been also reported for application in electrochemical supercapacitors [47]. To the best of the authors' knowledge, only one recent paper deals with ORR studies at Mn/PPy electrocatalysts prepared by electrosynthesis [36]. The process used in this work consists in a potentiostatic pulse-plating technique, elaborated after [36], that alternates anodic and cathodic polarisation. During the anodic pulse the electropolymerisation takes place together with the insertion of Mn<sup>II</sup> coordinated by pyrrolic nitrogen and the anodic oxidative deposition of MnO<sub>2</sub> nanoparticles, while the cathodic pulse potentially precipitates metallic and colloidal manganese hydroxide nanoparticles onto the undoped polymer. In this paper, we are concentrating on a selection of key physico-chemical aspects of the stability of the electrocatalytic properties of pyrolysed Mn/PPy. Specifically, the morphological and chemical modifications of the electrocatalyst surface under oxygen reduction in alkaline conditions have been monitored by quasi-in situ X-ray spectromicroscopy, after different stages of cyclic voltammetric ORR ageing at the sub-micron scale. To our knowledge, the stability of electrochemically synthesised Mn/PPy catalysts under operating conditions has been studied expressly here for the first time.

## 2. Material and methods

### 2.1. Electrochemical synthesis

Acetonitrile, MnCl<sub>2</sub>·6H<sub>2</sub>O and pyrrole were supplied by Aldrich. Before each electrodeposition run, the pyrrole monomer was distilled under rotary pump vacuum a few times (typically 3) until it became colourless. All the solutions were prepared with ultrapure water from a MilliQ system, exhibiting a resistivity of 18.2 MΩ·cm. The electrochemical syntheses were performed using a classical three-electrode cell with a graphite disc (Φ = 10 mm) as the working electrode (WE), a Pt wire spiral (5 cm<sup>2</sup>) as the counter electrode (CE) and an aqueous silver/silver chloride (Ag/AgCl/3M: 0.209 V/NHE) as reference electrode (RE), connected to the electrodeposition bath by a salt bridge. The liquid junction potential between aqueous and non-aqueous solutions has been checked to be negligible. All the potentials reported in the text as well as in the graphs and tables are referenced to the RHE scale. The electrochemical measurements were carried out at room temperature using ParStat and VersaStat potentiostats. The Mn/PPy catalysts were synthesised in de-aerated acetonitrile solutions containing 0.1 M pyrrole, 0.05 M MnCl<sub>2</sub>·6H<sub>2</sub>O, 1% v/v H<sub>2</sub>O and 0.1 M TBAP supporting electrolyte. The electrical programme used for electrodeposition was a step pulsed potential procedure elaborated on the basis of [36], consisting in the repetition of a cycle composed by: (i) an initial step at 0.976 V for 1 s to relax the compositional double layer; (ii) a subsequent anodic pulse at 2.176 V for 0.5 s to electrodeposit PPy as well as possibly Mn<sup>III</sup> and Mn<sup>IV</sup> species; (iii) a cathodic step at –0.824 V for 0.5 s to incorporate Mn<sup>0</sup> into PPy and (iv) a final anodic step at 2.176 V for 0.2 s to deposit another layer of PPy and Mn<sup>III,IV</sup>.

### 2.2. Micro-Raman spectroscopy

Micro-Raman spectra on pyrolysed Mn/PPy electrodes 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.

### 2.3. Pyrolysis procedure

The Mn/PPy catalysts electrodeposited on graphite were subjected to pyrolysis in a continuous flow reactor consisting of a quartz tube equipped with temperature control and a gas management manifold. N<sub>2</sub> at a flow rate 80 cm<sup>3</sup> min<sup>–1</sup> was used as carrier gas, under a slight overpressure with respect to ambient. After purging with N<sub>2</sub> for 10 min, the temperature was increased at a rate of 10 °C min<sup>–1</sup> and then kept constant for 2 h at 670 °C: this temperature value as been reported to maximise the ORR activity [36].

### 2.4. FE-SEM

The morphology and quality of Mn/PPy catalyst electrodeposited on graphite discs were investigated by using an NVISION 40 Zeiss Cross-Beam Focused Ion Beam (FIB) machine, equipped with a high resolution Gemini Field Emission Gun (FEG) scanning electron microscope column, with an ion column with Ga source and with an Oxford INCA 350 Xact Energy Dispersive X-ray Spectrometer (EDX). Quantitative image analysis was performed with the ImageJ software.

### 2.5. ORR electrocatalysis

ORR voltammetries on pyrolysed Mn/PPy/C electrodes were recorded in an O<sub>2</sub>-saturated (SIAD 6.0) 0.1 M KOH electrolyte at quasi-steady-state (5 mV s<sup>–1</sup>) and with a stagnant electrolyte. O<sub>2</sub> was bubbled for 20 min through the solution before the measurements and an O<sub>2</sub> blanket was kept above the electrolyte during voltammetry. For reference purposes, the same electrochemical experiments were duplicated with solutions that had been de-oxygenated by N<sub>2</sub> saturation.

### 2.6. SPEM

#### 2.6.1. Scanning photoelectron microscopy

Photoelectron microspectroscopy measurements were performed with the Scanning PhotoElectron Microscope (SPEM) hosted at the ESCA microscopy beamline at the Elettra synchrotron laboratory in Trieste, Italy. SPEM uses zone plate focusing optics providing a microprobe of diameter of ~100 nm and operates in both imaging and spectroscopy modes. Photoemission spectra of selected regions and chemical maps were acquired with 0.4 eV energy resolution by using 754 eV photon energy. More details about the microscope set-up and operation parameters can be found in [48,49].

#### 2.6.2. Set-up for quasi-in situ electrochemistry

The Mn/PPy sample is mounted on a UHV compatible transfer arm which allowed placing the electrode in contact with the electrolyte in a hanging-meniscus configuration, in order to run the electrochemical reactions, and to transfer it to the SPEM chamber without exposure to air. O<sub>2</sub> (SIAD) was allowed in the electrochemical chamber at 1 bar. The quasi-in situ analyses have been performed by sequentially transferring the sample – fixed on a sample-holder that bears an electrical connection allowing to use it as the WE – between the O<sub>2</sub>-pressurised electrochemical chamber – hosting a cell containing a 0.1 M KOH aqueous solution and equipped with Pt QRE and CE – to the UHV analysis chamber. More details on the set-up are provided in [50].

In order to gain information on the stability of catalysts subjected to prolonged ORR, SPEM and micro-XPS analyses have been conducted quasi-in situ by applying three representative sets of ageing conditions: 10, 35 and 100 voltammetric cycles in 0.1 M KOH at 5 mV s<sup>–1</sup> scan rate. The same area of the sample was recovered and the same locations could be analysed after each electrochemical treatment.

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