Optimization of a Fe−N−C electrocatalyst supported on mesoporous carbon functionalized with polypyrrole for oxygen reduction reaction under both alkaline and acidic conditions

*Luigi Osmieri, Alessandro H.A. Monteverde Videla, Stefania Specchia**

Politecnico di Torino, Department of Applied Science & Technology, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

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ABSTRACT

A series of Fe−N−C non-noble metal electrocatalysts for oxygen reduction reaction (ORR) are synthesized using mesoporous carbon (MPC) as C source, polypyrrole (PPY) as N source and Fe(II) acetate as Fe source. In the first part, the effects of the addition of poly-vinylpyrrolidone (PVP) and performing a heat treatment on the MPC-PPY support before the impregnation with Fe^{2+} ions are investigated. In the second part, the best catalyst obtained in the first part is used as a support, and the influence of a second pyrolysis treatment performed with or without further impregnation with Fe^{2+} is investigated. The materials are characterized by FESEM, TEM, EDX, BET-porosimetry, XPS, and FTIR. The electroactivity towards ORR is assessed with a rotating disk electrode (RDE) apparatus in both acidic and alkaline conditions. The different synthesis pathways examined have a direct influence on the ORR activity. The electroactivity and micropores content increases after the second heat treatment.

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Introduction

The high cost of Pt has been until now one of the main factors that have limited the widespread commercialization of the PEM fuel cell devices [1]. In particular, on the cathode of PEM fuel cells, a high amount of Pt has to be used, due to the sluggish kinetics of the oxygen reduction reaction (ORR) [2]. The slow kinetics of ORR leads to great overpotentials and lower energy conversion efficiency, making crucial the research toward non-precious metal based materials as ORR electrocatalysts in the alternative to Pt [3].

Several types of carbon-based materials containing nitrogen and transition metals have been found to be active towards ORR. The first studies were conducted in the 1960s on transition metals (Fe, Co) macrocyclic compounds like phthalocyanines and porphyrins [4]. In more recent years, many different synthesis strategies have been successfully adopted to obtain active Me−N−C (Me = Fe, Co, Cu, Mn, ecc.) ORR catalysts, using many different C supports, N-containing molecules, polymers or ammonia gas as N sources, and different transition metals ions [5−7].

Heat treatment at temperatures between 600 and 1000 °C in inert (Ar, N_2) or reactive (NH_3) atmosphere has been found to be very effective in increasing the ORR activity and stability of these materials [8]. Performing a second heat treatment also seems to have a positive effect [9,10].

Regarding the characteristics of the C support, it should have good electrical conductivity properties to assure a fast electron delivery to the active ensembles [11]. It should also have high specific surface area and high pore size distribution to favor the reactants and products transport self-directing to and from the active ensembles [12].

The use of N-containing polymers like polyaniline and polypyrrole (PPY), has been proved to be an been effective and cheap way to functionalize the surface of a carbon support with nitrogen atoms [13], or even to directly produce N-doped carbon materials without using any additional carbon support [14,15]. N-containing electro-conductive polymers (i.e., polyaniline, polypyrrole) were found to be active toward ORR even without performing any heat treatment [16—18]. However, after having been heat treated at high temperature under an inert atmosphere, the ORR electroactivity improves significantly, as well as the stability [9,19—22].

In this work, the synthesis of a noble metal-free Fe—N—C catalyst for ORR is optimized to obtain a more active catalyst. Inexpensive molecules (in comparison with Pt and more costly N-containing organic macrocyclic complexes) like sucrose and pyrrole are used as C and N sources, respectively. The first part of the optimization was the investigation on the effect of the addition of the N-containing surfactant polyvinylpyrrolidone (PVP) during the wet impregnation of the MPC-PPY support with Fe^{2+} ions. The use of surfactants in solution in synthesis procedures involving metal ions reduction and deposition with or without C-based supports has been found to be useful to achieve a better metal particles dispersion and distribution in different literature studies [23—25]. However, to the best of our knowledge, the effect of the use of PVP (as well as of other surfactants) in syntheses involving metal ions impregnation or complexation with N-containing molecules has not been investigated yet. The effect of performing a preliminary heat treatment before the wet impregnation with Fe ions was also investigated.

Afterward, in the second part, a further optimization was done, using as a support the best catalyst obtained in the first part. The influence of a second pyrolysis treatment performed with or without further impregnation with different amounts of Fe was investigated. The activities towards ORR in acid and alkaline conditions were measured using a rotating disk electrode (RDE) equipment. The catalysts activity varies depending on the different synthesis parameters. An evident ORR activity increase after the second heat treatment was found, and a direct correlation between the electroactivity and the catalyst surface area and micropores content was observed.

Materials & methods

Chemicals

Tetraethyl orthosilicate (TEOS, $\geq$98% purity), hydrochloric acid (37 wt.%), Pluronic P123® triblock copolymer, nitric acid (HNO_3, 70 wt.%), sulfuric acid (H_2SO_4, 98 wt.%), sucrose ($\geq$99.0% purity), hydrofluoric acid (HF, $\geq$40 wt.%), pyrrole (PY, $\geq$98% purity), ethanol ($\geq$99.8% purity), acetone ($\geq$99.8% purity), perchloric acid ($HClO_4$, 70 wt.%), potassium hydroxide (KOH, $\geq$85% purity), ammonium persulfate (APS, $\geq$99.8% purity), Nafion® 5 wt. % hydroalcoholic solution, iron(II) acetate (Fe(II)Ac, $\geq$99.99% purity) and polyvinylpyrrolidone (PVP, mw 10,000) were purchased from Sigma Aldrich. Nitrogen and oxygen gases were supplied in cylinders by SIAD with 99.999% purity. All aqueous solutions were prepared using ultrapure deionized water obtained from a Millipore Milli-Q system with resistivity >18 MΩ cm.

Synthesis

Synthesis of silica template
Mesoporous silica SBA-15 was prepared following the procedure reported by Zeng et al. [26], using the triblock copolymer EO20PO70EO20 (Pluronic P123) as a surfactant and TEOS as the silica source. In detail, 8.3 g of P123 was dissolved in 312 mL of 1.6 M HCl solution under stirring at 40 °C. Then, 19 mL of TEOS was added and the solution was stirred for 20 h keeping the temperature constant at 40 °C. Then, the temperature was increased at 100 °C and maintained constant for 24 h. The product was filtered, washed with deionized water, and calcined at 550 °C for 10 h under air to completely remove the surfactant.

Synthesis of mesoporous carbon
Mesoporous carbon (MPC) was synthesized using mesoporous silica SBA-15 via hard templating method [26]. Sucrose was used as the carbon source and the synthesis method consists on impregnating the SBA-15 silica with a solution containing sucrose and H_2SO_4. More in detail, a solution containing 10 mL of deionized water, 0.152 mL of H_2SO_4 and 2.5 g of sucrose was pipetted drop by drop onto 2 g of SBA-15. Then the temperature was increased at 100 °C on a hot plate, and kept constant for 6 h. Subsequently the temperature was increased to 160 °C and kept constant for 6 h more. This two-steps heating procedure is repeated after pipetting drop by drop a solution containing 10 mL of deionized water, 0.098 mL of H_2SO_4 and 1.6 g of sucrose. This further addition of solution was done to fill all the volume of the internal pores of the SBA-15 silica with the carbon precursor. Then, the carbon—silica mixture was heat-treated in a quartz-tube reactor at 830 °C for 6 h under nitrogen flow. To remove all the silica template, the mixture was dispersed in 110 mL of 5 wt.% HF solution. Finally, MPC was filtered under vacuum, washed with abundant deionized water and acetone, and dried in air.

In the following step, MPC was functionalized by reaction with concentrated H_2SO_4 and HNO_3 mixture, to introduce oxygen-containing functional groups (e.g. carbonyls, hydroxyls and carboxylic groups) on the MPC surface. 750 mg of MPC was introduced together with 120 mL of 1:1 vol. mixture of 98 wt.% H_2SO_4 and 65 wt.% HNO_3 into a triangular flask connected to a reflux apparatus. The flask was kept in reflux under stirring for 2 h. Then 400 mL of deionized water was added (this caused a fast temperature increase). The mixture was stirred and kept under reflux overnight. Then the functionalized MPC, called MPC_f, was filtered under vacuum, washed with abundant deionized water and dried in air. This surface functionalization should favor the pyrrole polymerization to take place preferentially on the MPC surface, due to the formation of hydrogen bonds between the oxygen-containing functional groups and the —NH groups of pyrrole [13].