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Performance of a Fe-N-C catalyst for the oxygen reduction reaction in direct methanol fuel cell: Cathode formulation optimization and short-term durability

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ABSTRACT

A non-noble metal (NNM) catalyst for oxygen reduction reaction (ORR) was synthesized using Fe(II)-phthalocyanine as unique source of Fe, N, and C, and SBA-15 ordered mesoporous silica as templating agent, resulting in a material with an extremely high specific surface area and a high microporosity (around 50%). FESEM, FTIR and Raman analyses were performed to investigate the morphology and the physicochemical properties of the catalyst. The ORR activity and the methanol tolerance were tested in rotating disk electrode (RDE), and the selectivity towards a complete 4-electrons reduction was investigated by rotating ring disk electrode (RRDE) test and hydrogen peroxide reduction test in RDE, showing very promising results. Thus, the Fe-N-C catalyst was tested at the cathode of a DMFC after determination of the optimal electrode formulation regarding catalyst loading and Nafion® content, showing a maximum power density of 20 mW cm^{-2} at 90 °C. A short term durability test to assess the behavior of both the Fe-N-C and the Pt/C catalysts was conducted on the DMFC, showing a better performance of the non-noble catalyst. Thus, the Fe-N-C catalyst is a potential good candidate to be used as catalytic material for DMFC cathode, in alternative to Pt. The performance in a H_2/O_2 PEMFC was tested as well, showing a power density of 105 mW cm^{-2} at 60 °C.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFC) are efficient chemical-to-electrical conversion devices that can operate close to ambient conditions [1]. For this reason, they are suitable for portable and automotive applications [2]. Among PEMFC, direct methanol fuel cells (DMFC) have gained particular attraction for portable applications (*i.e.* as power supply units for electronic devices) [3] as alternative to Li-ion batteries, or for powering remote off-grid devices like environment monitoring stations and back-up units for telecommunications [4]. The main drawbacks of DMFC are represented by the use of Pt-based catalysts at both the anode and the cathode, and the methanol crossover through the polymeric membrane, which dramatically affects both the durability and the performance [5]. Pt, in addition to its high cost [6], catalyzes both oxygen reduction reaction (ORR) and methanol oxidation reaction (MOR). Concerning ORR, high amounts of Pt are necessary at the cathode because of the sluggish kinetics of this reaction. On the other hand, concerning MOR, it is also a limiting step since Pt is poisoned by CO as reaction intermediate. Thus, the use of bimetallic Pt-Me (Me = Ru, Ir, Sn, Ni, ect.) is effective to reduce the CO poisoning effect [7]. Because of these problems, the research focused on the development of Pt-free catalysts for ORR [8]. Within several types of non-noble metal (NNM) catalysts for ORR, the most promising for low-temperature fuel cell application seem the carbon-supported transition metal/nitrogen (Me–Nx/C) materials (Me = Co, Fe, Ni, Mn, etc.) [9,10]. They have gained increasing attention due to their promising catalytic activity towards ORR, along with the utilization of abundant and inexpensive precursor materials [11]. In fact, since from 1964 transition metal macrocyclic molecules like porphyrins and phthalocyanines were investigated as ORR electrocatalysts [12,13]. However, they showed stability problems, as the decomposition of their structure in acidic media,

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resulting in a loss of catalytic activity. A significant breakthrough was achieved by performing a heat treatment at high temperature (600–1000 °C). During this heat treatment, a modification of the catalyst structure takes place, increasing the concentration of available ORR active ensembles while at the same time improving the catalyst stability [13,14]. Therefore, due to the modification of the structure after the high-temperature heat treatment, the use of transition metal macrocycle compounds was partially abandoned [15]. In fact, ORR active ensembles could also be formed starting from different precursors containing transition metals, nitrogen and carbon. For the production of ORR active ensembles, the presence of transition metal ions (Fe, Co, etc.), a source of carbon (carbon support, molecule, polymer), and a source of nitrogen (macrocycle, N-containing organic molecule or polymer, N-containing gas, i.e. NH_3) are required during the heat-treatment [16].

To improve both activity and stability of NNM catalysts, several different approaches have been explored. Among them, the optimization of synthesis conditions and procedures, the development of heat-treatment strategies, the development of alternative carbon supports, and the use of different transition metal complexes with N-containing ligand molecules as precursors [17–19].

To increase the density of the active ensembles, and at the same time have a high specific surface area (to assure good mass transport properties), a possible synthesis approach lies in avoiding the use of a carbon support [20,21], using a non-carbonaceous sacrificial support with an ordered structure (e.g. silica, alumina, zirconia). This sacrificial support is mixed with the precursor(s) containing nitrogen, carbon and transition metal, and it is removed after the pyrolysis. The resulting material is a “self-supported” Me-N-C catalyst (Me = Fe, Co, etc.) obtained as a negative replica of the templating sacrificial agent. As a result, the self-supported Me-N-C catalyst has high pore volume and good accessibility to the active ensembles [22–24].

In addition to the above-mentioned properties, this type of Me-N-C catalysts show very promising methanol tolerance and they do not suffer CO poisoning [9,25–27]. In fact, one of the fundamental features of an NNM catalyst is the high methanol tolerance, to be considered attractive for DMFC applications, and to replace Pt-based catalysts at the cathode. However, one of the major issues that are still limiting the application of NNM catalysts in DMFC is the durability [28], whose decrease seems to be ascribed to both active ensembles deactivation and mass transport problems due to cathode flooding [21,29,30].

In this work, we synthesized a Fe-N-C catalyst by impregnation of Fe(II)-phthalocyanine (Fe-Pc) on SBA-15 silica used as a hard-templating agent, resulting in a material showing a high specific surface area, and extremely rich in microporosity. The ORR activity of this catalyst, and the selectivity towards a direct complete 4-electrons reduction to H_2O, were assessed in a half-cell configuration by rotating disk electrode – rotating ring disk electrode (RDE-RRDE) technique, and performing a hydrogen peroxide reduction reaction (HPRR) test. Various MEA were prepared and tested in a 4 cm^2 single DMFC to optimize the Fe-N-C cathode formulation regarding catalyst loading and Nafion® content, and a short-term durability test in DMFC was performed. The performance of the Fe-N-C- catalyst was assessed in an H_2-fueled 4 cm^2 single PEMFC as well, for comparison purposes.

2. Experimental

2.1. Chemicals

Tetraethyl orthosilicate (TEOS, ≥ 98% purity), hydrochloric acid (HCl, 37 wt.%), Pluronic P123® triblock copolymer, hydrofluoric acid (HF, ≥ 40 wt.%), potassium hydroxide (KOH, 99.0% purity), ethanol (≥99.8% purity), acetone (≥99.8% purity), isopropanol (≥99.7% purity), Nafion® 5 wt.% hydroalcoholic solution, and iron(II) phthalocyanine $C_{32}H_{16}N_8Fe$ (Fe-Pc, 90% purity) were purchased from Sigma-Aldrich. Vulcan XC72R (BET specific surface area of 250 $m^2\,g^{-1}$, average particle size of 40–50 nm) was donated by Cabot Corp. Nitrogen and oxygen gases were supplied in cylinders by SIAD with 99.999% purity. Ultrapure deionized water obtained from a Millipore Milli-Q system (resistivity > 18 MΩ cm) was used throughout the experiments. All reagents were used as received without further purification. 20 wt.% Pt/C (HiSPEC™ 3000, Pt 20 wt.% on carbon black, Johnson Matthey), 40 wt.% Pt/C (HiSPEC™ 4000, Pt 40 wt.% on carbon black, Johnson Matthey) and 30 wt.% PtRu/C (HiSPEC™ 5000, Pt-Ru 30 wt.% on carbon black, Pt:Ru atomic ratio = 1, Johnson Matthey) were purchased from Alfa Aesar.

2.2. Synthesis of Fe-N-C catalyst

SBA-15 silica used as templating agent for the preparation of Fe-N-C catalyst was prepared in-house following a procedure described elsewhere [31].

Fe-N-C catalyst was prepared using Fe-Pc precursor as a unique source of Fe, N, and C. The complete synthesis procedure is described in our previous work [32]. Briefly, Me(II)-phthalocyanine was dissolved in an ethanol-water solution and wet-impregnated on SBA-15 silica (SBA-15 to Fe-Pc wt. ratio 1:1). After solvent evaporation, a pyrolysis was performed under inert atmosphere (N_2 gas flow) at 800 °C for 1 h. Then, the SBA-15 silica was removed by washing with 5 wt.% HF solution.

2.3. Physicochemical characterization

A field emission scanning electron microscopy (FESEM, model JEOL JSM 6700F) was used to investigate the morphology of the SBA-15 silica and the Fe-N-C catalyst.

Fourier transform infrared spectroscopy (FTIR) analysis was conducted on the Fe-N-C catalyst. Before the measurement, the powder of Fe-N-C was mechanically mixed with KBr and pressed. IR spectra were collected in air at 2 cm^{-1} resolution on a Bruker Equinox 55 FTIR spectrophotometer, equipped with an MCT (Mercury Cadmium Telluride) detector.

Raman spectroscopy was performed for the Fe-N-C catalyst to evaluate the ordered/disorder degree of its carbon-based crystalline structure, using a μ-Raman Spectroscopy μRS Renishaw InVia spectrometer equipped with a Leica DMLM confocal microscope and a CCD detector with an excitation wavelength of 785 nm (Renishaw plc, Gloucestershire, United Kingdom). The Raman scattered light was collected in the spectral range 100–1000 cm^{-1}). At least ten scans were accumulated in four different positions of the catalyst to ensure a sufficiently high signal to noise ratio.

2.4. RDE-RRDE electrochemical tests

For RDE and RRDE tests on the Fe-N-C catalyst, the ink was prepared by mixing 10 mg of catalyst powder with 150 μL of H_2O, 305 μL of isopropanol and 45.8 μL of Nafion 5% wt. solution. The ink was sonicated at 130 W for 30 min to achieve a good dispersion. With this formulation, the Nafion-to-catalyst mass ratio (NCR) is 0.2 and the catalyst density in the ink is 0.02 mg μL^{-1}. 4 μL of ink were micropipetted on the glassy carbon surface of the RDE, resulting in a catalyst loading on the electrode of 637 μg cm^{-2}.

As a comparison, a Pt catalyst (20 wt.% Pt/C) was also tested. In this case, the ink was prepared by dispersing 10 mg of catalyst (considering the total mass of Pt and C), 20 μL of deionized water, 33 μL of 5 wt% Nafion solution and 734 μL of isopropanol. The Pt loading on the electrode was 38 μg cm^{-2}.