Influence of the reaction temperature on the oxygen reduction reaction on nitrogen-doped carbon nanotube catalysts

Lai Truong-Phuoc [a,*], Cuong Duong-Viet [a,b], Won-Hui Doh [a,d], Antoine Bonnefont [c,*], Izabela Janowska [a], Dominique Begin [a], Elena R. Savinova [a], Pascal Granger [d], Cuong Pham-Huu [a,**]

[a] Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé (ICPEES), ECPM, UMR 7515 du CNRS, Université de Strasbourg, 25 rue Becquerel, 67087 Strasbourg Cedex 02, France
[b] Ha-Noi University of Mining and Geology, Dong Ngac, Tu Liem, Ha Noi, Viet Nam
[c] Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide, Institut de Chimie de Strasbourg (ICS), UMR 7177 du CNRS, Université de Strasbourg, 4, rue Blaise Pascal, CS 90032, F-67081 Strasbourg Cedex, France
[d] Unité de Catalyse et Chimie du Solide (UCCS), UMR 8181 du CNRS-Université de Lille-1, Bâtiment C3, Université Lille 1, 59655 Villeneuve d'Ascq Cedex, France

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ABSTRACT

Nitrogen-doped carbon nanotubes (N-CNT) were synthesized at 700 °C via the chemical vapour deposition (CVD) method and were used as catalysts in the oxygen reduction reaction (ORR) in 0.1 M KOH. The activity toward the ORR and the stability of these N-CNTs in alkaline solution were studied as a function of the reaction temperature and of the chemical treatment applied to the catalyst. The kinetic analysis of these catalysts was also carried out and compared to the ORR performance of the commercial Pt/C Vulcan XC72 catalyst. N-CNT-700BW catalyst without any chemical treatment after the CVD synthesis, possesses a half-wave potential $E_{1/2}$ of approximately 0.82 V vs. RHE, 50 mV lower than the $E_{1/2}$ value of Pt/C catalyst and a specific current density J_k at 0.9 V = 5.46 mA/mg at T = 25 °C. Removal of the major part of the iron growth catalyst by a chemical treatment resulted in a strongly decreased but still measurable activity. The activation energy of the N-CNT-based catalyst was calculated and is around 38 kJ mol^{-1} at an ORR overpotential of 300 mV. Increasing the temperature of the electrolyte up to 75 °C leads to a positive shift of the half-wave potential of the reaction as well as an increase of the H_2O_2 escape. The long-term stability test has also been conducted and indicates a good stability of the activity of the N-CNT-based catalysts under operation in alkaline media.

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1. Introduction

The oxygen reduction reaction (ORR) is of critical importance to support industrial development of fuel cells and metal-air batteries for the future energy mix infrastructure [1–3]. The slow kinetics of the ORR compared to that of the hydrogen oxidation at the anode severely limits the performance of low temperature fuel cells. To date, platinum-based materials are used as state-of-the art ORR catalysts due to their higher, compared to other materials, catalytic activity. However, they suffer from high cost, low tolerance to poi-sons such as methanol and CO, and low stability mostly due to the Pt particle agglomeration, Pt dissolution and to the corrosion of the carbon support under fuel cell operation conditions [4,5]. A large number of investigations have been devoted to the decrease of the amount and to the replacement of platinum by other catalysts, including Pt-based alloys [6–8], transition metal–nitrogen–carbon M–N–C catalysts [9–14], perovskite-type oxide catalysts [15–17] and carbon-based materials doped with various elements [18].

Application of M–N–C-type materials as the ORR catalysts dates back to the 1960–1970s when it was discovered that metal (e.g. Fe) porphyrins and Phthalocyanines can be pyrolyzed to produce highly active catalysts [19,20]. The last decades saw a remarkable rise in the interest toward the M–N–C ORR materials, a diversification of their methods of preparation by using various transition metal and nitrogen precursors [10,12,21] and a significant progress

in the understanding of the nature of the active sites and the mechanism of electrocatalysis [13,14,22].

Nitrogen-doped carbon composites such as nitrogen-doped carbon nanotubes/nanofibers and/or mesoporous carbon have received an increasing academic and industrial interest, as catalysts or as catalyst support with enhanced surface properties, in several catalytic applications during the last decades [23–28]. These composites, either in a bulk or supported forms, are mostly synthesized via chemical vapor deposition (CVD) process using different sources of carbon and nitrogen precursors and iron as the growth catalyst [29–35] or synthesized by pyrolysis of a precursor containing nitrogen, carbon in the presence of a transition metal catalyst [36,37]. Beside their use as catalyst support in several reactions, nitrogen-doped carbon nanotubes (N-CNTs) have also been considered as catalysts for replacing platinum in the cathode oxygen reduction reaction (ORR) for fuel cells application [38–44]. The issue on whether metal-free N-containing materials might act as catalysts in the ORR attracted much attention. It is widely accepted that while in alkaline media metal-free carbon materials possess the ORR activity, in acid the activity of metal-free materials is small. In recent studies, Singh et al. [45] and Masa et al. [46] compared N-containing carbon nanostructures and N-coordinated iron carbon catalysts and observed a significant positive effect of transition metal ions on the ORR activity. On the other hand, Singh et al. [45] reported that an initially a much higher activity of the iron-containing catalyst degraded more rapidly than that of iron-free catalyst in the fuel cell environment.

In general, the ORR is operated at temperature close to the maximum affordable temperature of the fuel cell membrane, ca. 80 °C for Nafion®. For the state-of-the-art anion exchange membranes the operating temperature is usually lower due to their so far insufficient thermal stability. It is thus of interest to compare the electrocatalytic activities of Pt and non-PGM (platinum group metal) catalysts as a function of the operation temperature. Furthermore, it is expected that an increase of the reaction temperature increases the materials corrosion which could directly impact the ORR performance during the operation. It is thus of interest to be able to correlate the stability of the N-doped carbon catalysts, after and before leaching of the iron catalyst with that of the Pt/C, not only at room temperature, but also at higher operating temperature. Deactivation of the Pt/C catalyst as a result of cycling was reported in a number of publications [5,43,44,47,48]. Herein, we report on the ORR activity and stability of the N-CNTs catalysts as a function of the reaction temperature (25–75 °C) and their comparison to a benchmark Pt-20 wt%/C catalyst. It is expected that such investigation will be of interest for the future development of non-PGM catalysts for fuel cell applications where the long-term stability is a prerequisite.

2. Experimental

2.1. N-CNTs synthesis

The N-CNT sample was synthesized using the chemical vapor deposition (CVD) method with iron supported on alumina as a growth catalyst [23,24,49]. The Fe/Al$_2$O$_3$ catalyst was synthesized by impregnating the gamma alumina support with an aqueous solution containing Fe(NO$_3$)$_3$ and contained 20 wt% of Fe. The solid was dried at room temperature overnight and oven-dried at 110 °C for 24 h. It was then calcined in air at 350 °C for 2 h in order to transform the nitrate precursor into Fe$_2$O$_3$ oxide. The Fe$_2$O$_3$/Al$_2$O$_3$ catalyst was housed in a quartz reactor localized inside an electric furnace. The catalyst was reduced under hydrogen flow (200 mL/min) at 400 °C for 2 h and then, the reaction temperature was raised (heating rate of 10 °C/min) to the synthesis temperature

and the H$_2$ flow was replaced by a C$_2$H$_6$/NH$_3$/H$_2$ mixture. The XRD patterns of the iron-based growth catalyst after calcination and reduction (not shown) confirm the complete reduction of the Fe$_2$O$_3$ phase. The C$_2$H$_6$ (Linde Gas, Germany), NH$_3$ (Air Liquide, France), and H$_2$ (Sol France) flow rates, used in the synthesis of N-CNT, were fixed at 50:50:20 sccm min^{-1}. The synthesis lasted 2 h, after that the reactor was cooled down to room temperature to provide the N-CNT-700BW sample. The N-CNT-700AW catalyst was obtained by subjecting the N-CNT-700BW sample to a sequence of alkaline (in 20 wt% NaOH solution at 80 °C for 24 h) and acid treatments (in 32 vol% HNO$_3$ at 80 °C for 24 h) in order to remove both the Fe growth catalyst and the Al$_2$O$_3$ support. Between the treatments the sample was thoroughly washed with Milli-Q water. Elemental analysis indicates that N-CNT-700BW and N-CNT-700AW contain about 1.5 and 0.12 at% of residual iron, respectively. The residual iron in N-CNT-700AW may be attributed to iron encapsulated within carbon nanotubes and thus not accessible to the acid during the acid wash.

2.2. Electrochemical measurements

Electrochemical studies were performed in a Teflon three-electrode cell in 0.1 M KOH supporting electrolyte in the temperature range from 25 to 75 °C, using Autolab PGSTAT30 (Eco Chemie, The Netherlands) potentiostat equipped with an analog linear sweep generator at the sweep rate of 10 mV s^{-1}. Mercury oxide (Hg/HgO) electrode and Pt-wire electrodes were used as reference and counter electrodes, respectively. Unless otherwise stated, all potentials hereinafter are referred to the reversible hydrogen electrode (RHE).

For the catalyst ink preparation, 10.0 mg of the catalyst sample, 5 mL isopropanol, and 50 μL Nafion solution (5 wt%) were ultrasonically mixed to form a homogenous catalyst ink. For the rotating ring disk (RRDE) measurements, the working electrode (PINE, AFE6R2GCPT) was prepared by loading 52.5 μL of catalyst ink onto a pretreated glassy carbon (GC) electrode (5.5 mm diameter and 0.2376 cm^2 geometric area) and then dried at room temperature. The catalyst loading was set at 445 μg cm^{-2} both for N-CNT-700BW and N-CNT-700AW samples. The benchmark Pt/C catalyst was charged with a 20 wt% Pt/C (Sigma) catalyst at a loading of 125 μg cm^{-2}.

All aqueous solutions were prepared using ultrapure water (18 MΩ cm, <3 ppb TOC) and supra-pure KOH (Sigma–Aldrich). In O$_2$-reduction experiments O$_2$ was constantly bubbled through the solution in order to maintain the saturation level and the ring potential was set at 1.2 V RHE in accordance with previous studies [43,50]. Collection efficiency (N) was calculated from the experimental data obtained in 10 mM K$_3$FeCN$_6$ in 0.1 M NaOH at 25 °C and the potential sweep rate of 10 mV s^{-1}. The collection efficiency was equal to 37% for the 20 wt% Pt/C Vulcan electrode in agreement with Chlistunoff [50].

The four-electron selectivity of the catalysts was evaluated based on the H$_2$O$_2$ yield, calculated from the following equation [50]:

$$H_2O_2 \ (\%) = 200 \frac{J_R/N}{J_R/N - J_D} \tag{1}$$

Here, J_D and J_R are the disk and ring current density, respectively, and N is the ring collection efficiency.

The apparent number of electrons transferred per O$_2$ molecule can be calculated in two ways. The first is to calculate it from the ring current as $n = -4J_D/(J_R/N - J_D)$. The second way is to use the first-order Koutecky–Levich equation:

$$\frac{1}{J_D} = \frac{1}{J_k} + \frac{1}{J_d} \tag{2}$$