Nitrogen doped carbon nanotubes (N-CNTs) were synthesized by modified chemical vapor deposition method using a novel two steps thermal technique. Pyridine was used as carbon and nitrogen source and ferrocene as catalyst for nanotubes growth. The effects of reactor temperature and carrier gas flow were investigated using scanning electron microscopy, transmission electron microscopy, Raman spectroscopy, X-ray photoelectron spectroscopy and linear scan voltammetry. Results show that the synthesis temperature and gas flow rate have influence on the physical, chemical and electrochemical properties of the nanostructures. Microscopy studies exhibit that synthesis temperature modify the length, yield and diameter of the N-CNTs. Transmission electron microscopy electron images show multiwalled carbon nanotubes with the typical bamboo like structures. High temperature and low flow rate generate more defects, as revealed by Raman analyses. N-CNTs synthesized at the highest temperature and flow rate show better electrocatalytic activity toward oxygen reduction reaction with promising lower onset potential and current densities up to 80% when compared to traditional Pt/C. The favorable performance is attributed to the higher nitrogen content and the type of nitrogen species, mainly pyrrolic and pyridinic incorporated in the carbon lattice.

For the last decades, platinum (pure and Pt alloys) has been the best and well known electrocatalyst for the oxidation and reduction reactions in fuel cells. However, scarcity, high price and degradation of platinum as catalyst in fuel cell represent a challenge for commercial proposes. In recent years, there have been efforts to reduce the platinum loading, or even to eliminate it from the electrodes. It is therefore necessary to develop non-Pt catalytic materials available, cheap and electroactive to replace the precious metal. Carbon nanotubes doped with nitrogen (N-CNTs) have reached the point to become an alternative catalyst for oxygen reduction reaction (ORR) in fuel cells cathode. There have been many studies concerning the synthesis of carbon nanotubes doped with nitrogen atoms using different carbon-nitrogen precursors using chemical vapor deposition (CVD) method and having a good electrocatalytic activity for oxygen reduction. Alexeyeva synthesized N-CNTs using acetonitrile as carbon and nitrogen sources. They studied the electrocatalytic reduction of oxygen with and without doped nanotubes in 0.5M H₂SO₄ solution where the N-CNTs show significantly more activity for ORR than the free-doping nanotubes. Wong obtained N-CNTs through CVD technique using three different chemical precursors as nitrogen sources: aniline (A), diethylamine (DEA) and ethylenediamine. The analysis revealed that the N-CNTs obtained from EDA with 6.5 at. % N was more active for ORR in acidic medium than nanotubes from A and DEA with 5.9 at. % N and 4.3 at. % N, respectively. Other studies have also showed the important role of nitrogen precursors on the N-CNTs structure. Nevertheless, few studies have been made on the different synthesis conditions of N-CNTs and the impact to improve the electrocatalytic properties for ORR. This work presents the production of N-CNTs by Modified Chemical Vapor Deposition (M-CVD) using pyridine as nitrogen and carbon source and the electrochemical study of the effects of two parameters, such as the synthesis temperature and carrier gas flow. The materials were evaluated toward the ORR by linear sweep voltammetry measurements using a catalyst-coated rotating disk electrode at different rotation rates in acid media.

N-CNTs synthesis.—The synthesis of N-CNTs was carried out by the M-CVD method and it is shown in Figure 1. A solution with Pyridine (99.5%, Merck, carbon and nitrogen source) and Ferrocene (98%, Aldrich, metal catalyst) were mixed. Two step synthesis processes were used; first the solution was pre-heated in a home-made vaporizer connected to a tubular furnace where the synthesis takes place. Argon is used as carrier gas and Vycor tube as substrate. After synthesis, the furnace was cooled down and the final products were removed from the inside of the Vycor tube. Before the electrochemical characterization, N-CNTs were treated with concentrated nitric acid in a reflux system for 12 h. The carrier gas flow rate and the synthesis temperature were the two variables considered for the parametric study, with two levels each one (low and high). Table I shows the labelling used to name the samples. A total of 4 experiments were carried out in order to know the effects of the two different factors on the electrocatalytic performance of N-CNTs.

Physical and chemical characterization.—Scanning electron microscopy (SEM) was carried out to determine the morphology of N-CNTs using a Vega 3 system from Tescan. Different random areas were selected to have a statistical approach. Energy-dispersive X-ray spectrometer (EDS) attached to the SEM was used to determine chemical composition of each sample. Several random measurements were carried out in order to know the effects of the two different factors on the electrocatalytic performance of N-CNTs.

![Figure 1. Scheme of the modified chemical vapor deposition system.](image-url)
gathered from different sample areas to have a representative approach of the elemental analysis. Transmission electron microscopy (TEM) imaging was performed on a JEOL JEM-2200FS to provide high-resolution images of the samples. Raman spectroscopy (LabRAM He-Ne laser 632.8 nm with resolution of 1 cm<sup>-1</sup>) was utilized for investigating the first order Raman scattering of the samples and to know the degree of structural defects present. Element composition and chemical states of the elements were obtained by means of an XPS spectrometer from SPECS GmbH, equipped with a PHOIBOS 150 WAL hemispherical analyzer and a monochromated X-Ray source (μ-FOCUS 500) utilizing the radiation of Al Kα (hv = 1.486.7 eV). Measurements were performed under ultra-high vacuum conditions with a working pressure lower than 2 × 10<sup>-9</sup> Torr. Samples were mounted on a sample holder and kept overnight in high vacuum in the preparation chamber before they were transferred to the analysis chamber of the spectrometer. XPS survey spectra were obtained for a wide binding energy range with a 1 eV step size, while high-resolution spectra were acquired with a 0.1 eV step size, dwell time of 0.2 s, and were scanned with several sweeps until a reasonable signal-to-noise ratio was observed (20–50 scans). Spectra are presented without smoothing.

Oxygen reduction reaction activity evaluation.—The electrochemical evaluation was carried out in a rotating disk electrode (RDE) from BASI and coupled to an Epsilon potentiostat/galvanostat to control the speed and acquire the data. A conventional three electrodes cell arrangement was used. Glassy carbon electrode (0.07 cm<sup>2</sup>), Ag/AgCl (saturated in 3 mol L<sup>-1</sup> KCl) electrode, and a platinum wire, were used as working, reference and counter electrodes, respectively. Glassy carbon electrode (0.07 cm<sup>2</sup>) was utilized for investigating the first order Raman scattering of the samples and to know the degree of structural defects present.

Elemental composition and chemical states of the elements were obtained by means of an XPS spectrometer from SPECS GmbH, equipped with a PHOIBOS 150 WAL hemispherical analyzer and a monochromated X-Ray source (μ-FOCUS 500) utilizing the radiation of Al Kα (hv = 1.486.7 eV). Measurements were performed under ultra-high vacuum conditions with a working pressure lower than 2 × 10<sup>-9</sup> Torr. Samples were mounted on a sample holder and kept overnight in high vacuum in the preparation chamber before they were transferred to the analysis chamber of the spectrometer. XPS survey spectra were obtained for a wide binding energy range with a 1 eV step size, while high-resolution spectra were acquired with a 0.1 eV step size, dwell time of 0.2 s, and were scanned with several sweeps until a reasonable signal-to-noise ratio was observed (20–50 scans). Spectra are presented without smoothing. Charge referencing was done against adventitious carbon by setting the C1s peak maximum at 284.5 eV. The chemical state has been evaluated by curve fitting the corresponding energy region using a minimum number of doublets. Spectra were decomposed with the Casa XPS program (Casa Software Ltd., UK) by using a Gaussian/Lorentzian (70/30) product function after subtraction of a linear background. Relative atomic concentrations and ratios were calculated by using peak areas and normalized on the basis of acquisition parameters and tabulated sensitivity factors.

### Table I. Synthesis parameters and labels of N-CNTs.

| FACTORS                          | Value | Label | Value | Label |
|----------------------------------|-------|-------|-------|-------|
| Carrier gas flow rate (L min<sup>-1</sup>) | 0.5   | A     | 1     | B     |
| Reactor temperature (°C)         | 800   | 8     | 900   | 9     |

**Results and Discussion**

Figure 2 shows representative SEM images of N-CNTs samples prepared at a) 800°C and b) 900°C. Additionally, N-CNTs synthesized at 900°C show larger yields than those prepared at 800°C, which is in agreement with results from Chizari.

The morphology of N-CNTs was also studied by HRTEM as shown in Figure 3. Multiwall carbon nanotubes are identified in both cases. Bamboo-like structures are observed, which is the typical carbon arrangement of nanotubes when doped with nitrogen. The outer diameter of N-CNTs ranges were 53–64 nm and 67–96 nm for 800°C and 900°C samples, respectively. Higher temperature increases the outer diameter of the nanotubes due to increments of the Fe particle diameter. Scanning and transmission electron microscopies did not show evidence of effects of the flow rate.

Relative elemental atomic composition analysis using SEM-EDS indicated the presence of carbon, iron, nitrogen and oxygen, as shown in Table II. This analysis demonstrates the presence of nitrogen with similar atomic ratio in all samples. The nitrogen content correlated with the bamboo-like structure typical in nitrogen carbon doped, which indicated an evidence that nitrogen is into the carbon lattice. Raman spectroscopy measurements are presented in Figure 4. Two main characteristic peaks around 1333 cm<sup>-1</sup> and 1588 cm<sup>-1</sup>, corresponding to respective D and G bands, are clearly noticed. Band D, known as the band of disorder, is caused by atomic displacement and lattice defects, while G band indicates the formation of well graphitized nanotubes. An I<sub>D</sub>/I<sub>G</sub> ratio close to zero suggests an ordered structure of carbon, while a large ratio indicates the presence of more defects in the carbon nanotubes. The obtained average values for I<sub>D</sub>/I<sub>G</sub> and I<sub>C</sub>/I<sub>G</sub> ratios of N-CNTs samples are included in Figure 4. In the pristine carbon nanotube, the D band intensity is slightly smaller than the G band intensity, indicating some degree of graphitization or few defects. On the other hand, in all nitrogen doped CNTs samples, D band intensity is greater than G band. As expected, any distortion in the hexagonal lattice of pure carbon will result in an increase in D band intensity. In fact, data show a clear increment in the I<sub>D</sub>/I<sub>G</sub> ratio of N-CNTs as compared to pristine CNT, indicating more defects in the carbon structure. This
Table II. Relative elemental composition obtained by SEM-EDS.

| Sample Name | C at. % ± | Fe at. % ± | N at. % ± | O at. % ± |
|-------------|-----------|------------|-----------|-----------|
| A8          | 80.48     | 0.18       | 5.43      | 7.88      |
| B8          | 87.97     | 0.42       | 4.29      | 6.42      |
| A9          | 87.49     | 0.55       | 4.91      | 5.94      |
| B9          | 84.55     | 0.36       | 5.6       | 8.55      |

*Sample names were configured as explained in Table I.

Figure 4. Raman spectra of pristine CNT and N-CNTs.

The phenomenon can be explained by the integration of nitrogen atoms in the structure of the nanotubes, which reduces the ordering of the graphitic network. Comparing the mean values of the N-CNTs ID/IG ratio at different temperatures, it can be noticed the samples grown at 900 °C to have a larger ratio than those prepared at 800 °C. This means that nanotubes prepared at higher temperature produce more structural defects. The gas flow rate effect can also be appreciated since the lower the flow rate, the higher the number of structural defects. On the other hand, there is a band, around 2657 cm⁻¹, which is normally referred to band G’ (or 2D). This is an overtone of the D band and the intensity ratio IG'/IG can be used as a measurement of a degree of crystallinity. The IG'/IG intensity ratio shows that the degree of crystalline perfection of N-CNTs decrease considerably with respect to pristine CNT due to the incorporation of nitrogen into the carbon lattice.

Hydrodynamic behavior of selected N-CNTs samples was evaluated by linear sweep voltammetry to determine oxygen reduction reaction (ORR) performance and results are presented in Figure 5. Figure 5a shows polarization curves at different rotation speeds, in oxygen saturated 0.5 M H₂SO₄. Magnitude of current density

Figure 5. Linear sweep voltammograms for ORR of N-CNTs in O₂-satured 0.5 M H₂SO₄ and scan rate of 5 mV s⁻¹. a) Sample B9 at several rotation speeds; b) all samples at 1600 rpm.
Figure 6. XPS N 1s spectra of N-CNTs samples a) B8 and b) B9.

increases steadily as a function of rotation speed, between 100 and 2500 rpm, revealing the ORR. Figure 5b shows linear sweep voltammograms of studied samples and their comparison with pristine CNT and 20% Pt/C, respectively. Pristine CNT exhibits the lowest current density and a limiting current plateau is not formed, indicating poor or lack of ORR activity, normally showed for unmodified carbon materials. All the N-CNTs samples showed ORR activity. The onset potential presented on B9 sample is about 0.84 V/SHE, a value lower than 0.9 V/SHE of commercial 20 wt% Pt/C. The slight increase in the activation energy indicates that the N-CNTs possess a good ORR electrocatalytic activity regarding the onset potential and it opens a good area of study, since the non Pt materials are comparable to the one with high precious metal loading. The onset potential value achieved in B9 sample is slightly higher than other values reported in the literature. Mo synthesized N-CNTs at different temperatures (750–950 °C) using imidazole and the maximum potential gotten was 0.75 V/SHE in 0.5 M H2SO4. Alexseyeva4 studied ORR of N-CNTs synthesized at 800 °C from acetanilide, getting an E0/2 = 0.74 V/SHE, also performed in acidic media. Similarly, Vikkisk20 prepared N-CNTs at 750 °C from urea, obtaining an E0/2 = 0.59 V/SHE, using also 0.5 M H2SO4, Qu21 treated carbon nanotubes (undoped) with ammonia, and found that ORR starts at 0.72 V/SHE. Furthermore, Dorjgotov28 synthesized N-CNT from ethylenediamine at different temperatures (600–900 °C) and the results showed an onset potential of 0.83±0.01 V/SHE. These studies reveal that the type of chemical precursor determines the nature of nitrogen bonding on the surface of N-CNTs, which significantly affects the onset potential.2 The higher value of onset potential from the N-CNTs reported in this work can be attributed to the particular molecular structure of pyridine and the nitrogen – carbon bond originated.

The limiting current density for determining the catalytic material performance toward the ORR was also studied. Based on polarization curve results, sample B9 exhibited the highest ORR activity among the synthesized samples. The maximum current density reached from this non-Pt catalyst at 0.4 V vs SHE was 80% compared with traditional Pt/C, and this sample also showed a more negative onset potential. Hence, N-CNTs, under synthesis conditions of B9 sample, can be considered as a good electrocatalyst candidate in cathodes for polymer electrolyte fuel cells (PEMFC).

N-CNTs samples synthesized at 900 °C exhibit limiting current densities higher than samples prepared at 800 °C, which indicate that the N-CNTs grown at higher temperature show better electrocatalytic activity. The ORR results are consistent with Raman spectroscopy measurements, where the synthesis temperature plays an important role, because the higher the temperature more defects are generated in the carbon structure; it can be attributed to the increment of the nitrogen content, resulting a higher catalytic activity. The effect of temperature on the catalytic activity of the N-CNTs under acidic conditions (0.5 M H2SO4) has been reported.25,26,28 Dorjgotov28 evaluated the catalytic activity of N-CNTs and show the synthesis temperature (600–900 °C) to affect significantly the limiting current density; samples at 900 °C exhibited greater jL and therefore better catalytic activity. Wang27 prepared N-CNTs at 900 °C from Iron (II) phthalocyanine, where the jL was 2.3 mA cm−2 at 0.2 V/SHE. Other studies (different from 0.5 M H2SO4) also show that high pyrolysis temperature increases jL.

The flow rate of argon gas (during the synthesis) also shows a significant effect on the current density. Normally, in a CVD process the carrier gas is used to feed precursor sources and catalyst into the reactor. The polarization curves of N-CNTs show that the higher the gas flow rate the higher jL values are obtained when are compared at the same temperature. Although scarce research has been reported on the effect of carrier gas in the physical properties of CNT,31–34 no evidence was found over the electrochemical properties. Hence, this studies reveal the importance of the gas flow rate on the electrocatalytic properties of N-CNTs.

Elemental surface composition and identification of different nitrogen groups in N-CNTs was obtained by XPS measurements. Figure 6 shows high-resolution nitrogen 1s energy region (in eV units) of selected N-CNTs samples prepared with a gas flow of 1 L min−1. Five different types of nitrogen species were identified. The peak at 398.6–399.9 eV is unambiguously assigned to pyridinic nitrogen with the sp2-hybridized nitrogen atoms, which are bonded to two carbon atoms.12,13,35 The peak at 400–400.5 eV corresponds to nitrogen in the form of nitrogen oxides of pyridinic nitrogen existing as pentagonal pyrrolic nitrogen.5,16,18 The peak at 401.5–403.1 eV, can be attributed to the quaternary or graphitic-like nitrogen, which are the highly coordinated nitrogen atoms substituting carbon atoms on the graphene layers and bonded each to three carbon atoms.10,12,13,35 The peak at 406.1–407.3 eV corresponds to gaseous nitrogen (N2), which is encapsulated in the cavities of nanotubes or absorbed on the surface of tube walls.6,10,41,42

Table III shows the surface relative atomic composition (at. %) of selected N-CNTs detected by XPS. The overall nitrogen content of all samples synthesized at 900 °C was higher than that those prepared at 800 °C. The signal corresponding to pyrrolic nitrogen is equal from a cleaning treatment with HNO3 to remove impurities; carbon chemical oxidation generated therefore oxygen-containing groups on the carbon surface, as quinone groups.38–40 The peak at 406.1–407.3 eV corresponds to gaseous nitrogen (N2), which is encapsulated in the cavities of nanotubes or absorbed on the surface of tube walls.6,10,41,42
best ORR activity, this high activity can be attributed to the relative highest atomic concentration of pyrrolic and pyridinic species. The results obtained are consistent with those acquired from Raman spectroscopy. At higher temperatures, higher nitrogen concentration was obtained and, therefore, greater structural defects (due to larger ratio \( I_D/I_G \)) are generated in the nanotubes. The behavior of \( I_D/I_G \) ratio as a function of nitrogen doping in the N-CNT is well documented in the literature. In agreement with some previous reports, pyridinic nitrogen is responsible for the catalytic activity in N-CNTs in acidic medium, while other authors suggest that quaternary nitrogen as the responsible for ORR. In many reports is widely accepted that N-doping in carbon nanotubes is an important factor for their electrocatalytic behavior during ORR. However, it is still controversial which type of N doping is the real active site for ORR.

**Conclusions**

Multiwalled carbon nanotubes doped with nitrogen, using pyridine as agent, were successfully synthesized using a thermal two-stage modified chemical vapor deposition method. The synthesis temperature and carrier gas flow rate parameters showed to be important on the physical, chemical and electrochemical properties. The variables have a positive influence in the length and diameter of the carbon nanotube, synthesis yield, nitrogen content and structural defects. The results show evidence that nitrogen was incorporated into the carbon lattice as pyrrolic and pyridinic species, mainly. This incorporation allows good electrocatalytic activity toward ORR. Lower onset potential and current densities comparable with platinum basis materials, place the N-CNTs synthesized as a good non-precious metal electrocatalyst candidate for cathode fuel cells.

**Acknowledgments**

The authors acknowledge the support provided by CONACYT(Mexico)–CNPq(Brasil) under grant No. 174689. They also would like to thank David A. Domínguez for valuable XPS measurements and Carlos Ornelas and Pedro Pisa from NANOTECH (CIMAV) for their technical support in HRTEM and Raman Spectroscopy. Finally, Y. Verde Gómez thanks to PRODEP.

**References**

1. Z. Chen, D. Higgins, H. Tao, R. S. Hsu, and Z. Chen, The Journal of Physical Chemistry C, 113, 21008 (2009).
2. W. Wong, W. Daud, A. Mohamed, and A. Kadhum, International Journal of Hydrogen Energy, 38, 9421 (2013).
3. Y. Wang, X. Cui, Y. Li, L. Chen, H. Chen, L. Zhang, and J. Shi, Carbon, 68, 232 (2014).
4. A. Alexeyev, E. Shulga, V. Kizand, I. Kink, and K. Tammeveski, Journal of Electroanalytical Chemistry, 648, 169 (2010).
5. C. Chen, J. Zhang, R. Wang, D. Su, and F. Peng, Chinese Journal of Catalysis, 31, 948 (2010).
6. C. Wang, Z. Huang, L. Zhan, J. Yang, W. Qiao, X. Liang, and L. Ling, Diamond & Related Materials, 20, 1353 (2011).
7. J. Q. Huang, M. Q. Zhao, Q. Zhang, J. Q. Nie, L. D. Yao, D. S. Su, and F. Wei, Catalysis Today, 186, 83 (2012).
8. D. Higgins, Z. Chen, and Z. Chen, Electrochimica Acta, 56, 1570 (2011).
9. J. Moulder, W. Stickel, P. Sobol, and K. Bomdén, Handbook of X-ray Photoelectron Spectroscopy, p. 253, Perkin-Elmer corporation, Minnesota (1998).
10. K. Chizari, Z. Chen, M. Houllé, I. Florea, P. Bernhardt, M. J. Ledoux, and C. Pham-Huu, Applied Catalysis A, 380, 70 (2010).
11. M. Mauzener, M. A. Mamo, E. N. Nxumalo, W. A. Otterlo, and J. N. Coville, Synthetic Metals, 162, 2307 (2012).
12. J. Bao, N. Kishi, I. Khati, and T. Soga, Materials Letters, 113, 114 (2013).
13. K. Chizari, U. Sundararaj, A. Vena, and L. Laurentius, Carbon, 48, 369 (2014).
14. J. Liu, Y. Zhang, M. Ioan Ionescu, R. Li, and X. Sun, Applied Surface Science, 257, 7837 (2011).
15. S. D. Mhlanga, E. N. Nxumalo, N. J. Coville, and V. V. Srinivasu, Materials Chemistry and Physics, 130, 1182 (2011).
16. C. Xiong, Z. Wei, B. Hu, S. Chen, L. Li, L. Guo, W. Ding, X. Liu, W. Ji, and X. Wang, Journal of Power Sources, 215, 216 (2012).
17. J. Sesquipia, S. Panda, and C. Jacob, Bulletin of materials science, 32, 135 (2009).
18. K. Ghosh, M. Kumar, T. Maruyama, and Y. Ando, Carbon, 48, 191 (2010).
19. Y. Shao, J. Sun, G. Yin, and Y. Gao, Applied Catalysis B: Environmental, 79, 89 (2008).
20. A. Palca, K. Ikeda, T. Masuda, and K. Uosaki, Journal of Power Sources, 220, 20 (2012).
21. S. Chaisitsak, J. Nuekaw, and A. Tuantranont, Diamond & Related Materials, 16, 1558 (2007).
22. B. Escobar, R. Barbosa, M. Miki Yoshida, and Y. Verde Gomez, Journal of Power Sources, 243, 88 (2013).
23. A. J. Bard and L. R. Faulkner, Electrochemical Methods, p. 92, John Wiley & Sons, New York (2001).
24. F. V. Rodríguez Varela, A. Solorza Feria, and E. Hernández Pacheco, Celdas de combustible, p. 39, Canada (2010).
25. Z. Mo, S. Liao, Y. Zheng, and Z. Fu, Carbon, 50, 2629 (2012).
26. M. Vikkisk, J. Krusenbus, U. Joost, E. Shulga, and K. Tammeveski, Electrochemistry Acta, 87, 709 (2013).
27. Y. Qiu, J. Yin, H. Hou, J. Yu, and X. Zuo, Electrochimica Acta, 96, 225 (2013).
28. A. Dorigovot, J. Ok, Y. Jeon, S.-H. Yoon, and Y. Gun Shin, Journal Appl Electrochem, 43, 387 (2013).
29. C. H. Choi, S. Y. Lee, S. H. Park, and S. I. Woo, Applied Catalysis B: Environmental, 103, 362 (2011).
30. T. C. Nagahara, S. Kundu, M. Bron, M. Muller, and W. Schuhmann, Electrochemistry Communications, 12, 338 (2010).
31. S. Chaisitsak, J. Nuekaw, and A. Tuantranont, Diamond & Related Materials, 16, 1558 (2007).
32. A. Barreiro, C. Kramberger, M. Rummeli, A. Gruneis, D. Grimm, S. Hampel, T. Gemming, B. Buchner, A. Buchhold, and T. Pichler, Carbon, 45, 55 (2007).
33. S. K. Srivastava, K. Sanjay, V. Vankar, and V. Kumar, Thin Solid Films, 515, 1552 (2006).
34. C. H. See, K. J. MacKenzie, O. M. Dunen, and A. T. Harris, Chemical Engineering Science, 64, 3614 (2009).
35. G. N. Ilinich, B. L. Moreo, N. A. Rudina, I. P. Prosvirin, and V. I. Bukhtiyarov, Carbon, 50, 1186 (2012).
36. S. Kundu, W. Xia, W. Busser, M. Becker, D. A. Schmidt, M. Havenith, and M. Muller, Physical Chemistry Chemical Physics, 12, 4351 (2010).
37. E. Ibrahim, V. O. Khavrus, A. Lonnhardt, S. Hampel, S. Oswald, M. H. Rümmeli, and B. Buchner, Diamond & Related Materials, 19, 1199 (2010).
38. N. P. Subramanian, X. Li, V. Nallathambi, S. P. Kumaraguru, H. Colon-Mercado, G. Wu, J. W. Lee, and B. N. Popov, Journal of Power Sources, 188, 39 (2009).
39. Y. Verde, G. Alonso, V. Ramos, H. Zhang, A. J. Jacobson, and A. Keer, Applied catalysis A, 277, 201 (2004).
40. E. N. Nxumalo, P. J. Letsoalo, L. M. Cele, and N. J. Coville, Journal of Organometallic Chemistry, 495, 2596 (2010).
41. D. C. Higgins, J. Wu, L. Li, and Z. Chen, Electrochimica Acta, 59, 8 (2012).
42. E. Xu, J. Wei, K. Wang, Z. Li, X. Gui, Y. Jia, H. Zhu, and D. Wu, Carbon, 48, 3097 (2010).
43. S. Maltonado, S. Morin, and K. J. Stevenson, Carbon, 44, 1429 (2006).
44. T. Sharif, F. Nitze, H. R. Barzag, C.-W. Tai, M. Mazurkiewicz, A. Malolepszy, L. Stobinski, and T. Wagberg, Carbon, 50, 3535 (2012).
45. R. Zhang, Y. Peng, Z. Li, K. Li, J. Ma, Y. Liao, L. Zheng, X. Zuo, and D. Xia, Electrochimica Acta, 147, 543 (2014).