The use of a dynamic hydrogen electrode as an electrochemical tool to evaluate plasma activated carbon as electrocatalyst support for direct methanol fuel cell

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ABSTRACT

The objectives of this study were to functionalize the carbon black surface by chemically introducing oxygenated groups using plasma technology. This should enable a better interaction of the carbon support with the metallic catalyst nanoparticles, hindering posterior support particle agglomeration and preventing loss of active surface. PtRu/C nanoparticles were anchored on the carbon supports by the impregnation method and direct reduction with hydrazine. Physical characterization of the materials was carried out using energy dispersive X-ray analysis and transmission electron microscopy. The screen printing technique was used to produce membrane electrode assemblies for single cell tests in methanol/air (DMFC). Tests were carried out using the dynamic hydrogen electrode as an electrochemical tool to evaluate the anode and cathode behavior separately.

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1. Introduction

Carbon black is frequently used as catalyst support in polymer electrolyte membrane fuel cells (PEMFCs) [1,2] and direct methanol fuel cells (DMFCs) [3–6], because of its relative stability in both acid and basic media, good electronic conductivity and high specific surface area. The support material has a strong influence on the properties of the catalysts, such as metal particle size, electrochemical active area and size distribution. Furthermore, degree of alloying, stability, mass transport and electronic conductivity of the catalyst layer are also affected by the chosen support material. Hence, development of carbon supports plays an important role for the future PEMFC and DMFC technology. The support should be properly selected, with a suitable specific surface area, porosity, morphology, surface functional groups and electronic conductivity. Corrosion resistance is also a crucial parameter to be considered, while developing an active commercial catalyst. Most of these parameters are affected by the process used to prepare the carbon black. Carbon black still reveals inadequacies for this purpose [7,8]. One approach would be the chemical modification of the surface of the carbon black support used to anchor the nanoparticles of the electrocatalysts. Chemical reactions could be applied to encapsulate, protect and change the hydrophobic/hydrophilic character of the carbon materials. By this means, the reactivity can be changed, catalytic properties modified, as well as composites created and polarity changed (zeta potential) [9–12]; or by using plasma activation.

In this study, treatment of the carbon black surface with plasma technology [13–16] with Ar–O_2 atmosphere was carried out. The treatment introduces oxygenated functional groups, modifying its properties, hindering both posterior agglomeration and loss of active surface. PtRu electrocatalysts were prepared by an impregnation method and direct reduction with hydrazine [17,18]. The screen printing technique was used to produce membrane electrode assemblies (MEAs) for single cell tests in methanol/air (DMFC) [17–19].

In fundamental studies of PEMFCs, it is necessary to measure the single electrode potentials in order to understand the distribution of the voltage losses. However, there are some

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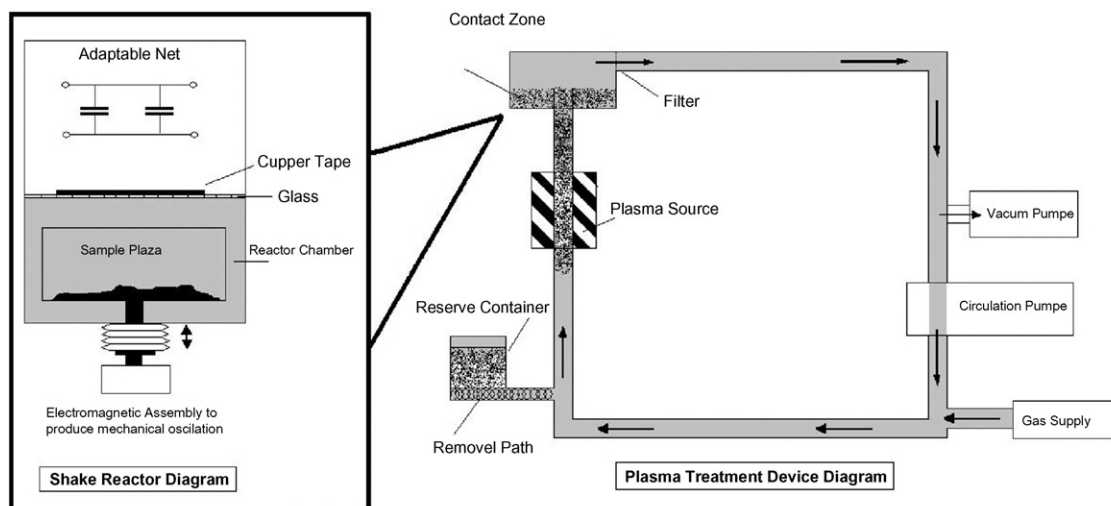E-mail address: marcelocarmo1@gmail.com (M. Carmo).

Fig. 1. Model of the plasma activation system utilized for carbon black XC-72 treatment.

difficulties in mounting a reference electrode to the MEA due to the geometric restriction. Because the electrolyte membrane is thin and the current density is high, it is hard to eliminate the *iR* drop in the electrolyte membrane. Furthermore, due to the long distance between the reference electrode and the working electrodes (gas diffusion electrodes) that may produce a potential drift caused by the uneven distribution of water or temperature, it is preferred that the reference electrode be positioned as close as the working electrodes, especially in the case of measuring the potential distribution in the electrolyte using several reference electrodes [20]. Hence, the use of a suitable reference electrode for evaluating the cell performance and behavior is crucial for PEMFC and DMFC technology development [21–23]. The use of a three-electrode cell system would demand a reference electrode design with special geometry, concerning a uniform current density at the working electrode; otherwise different regions of the working electrode will present different potentials, and the measured data may be misleading [23,24]. The reference electrode should be placed in a uniform potential region, and the distance between the reference electrode and the working electrodes should be at least three times the thickness of the polymer electrolyte layer in order to avoid potential gradients along the electrolyte surface and make the measurement insensitive to the exact location of the reference electrode [25]. Another requirement for electrochemical measurements is that the cathode and anode should be perfectly aligned with each other to avoid uneven current distribution [25]. Problems could occur in the case of dehydration of the membrane outside the active region [26], but the use of a proper cell design and proper humidification cell system should avoid these problems [27].

The dynamic hydrogen electrode (DHE) has emerged as the most promising and suitable electrolyte design to be used as a reference electrode in DMFC [26,27]. In a DHE, the hydrogen is produced at the Pt wire with the application of a small cathodic current, in the range of 6 μA, such that the coverage of hydrogen on the electrode can be considered constant, resulting in a stable reference potential. Advantages of the DHE include minimal contamination of the measured system and no need for a salt bridge [26].

In this work, the use of plasma activated carbon as electrocatalysts support and the first procedures to use and

discuss properly the results of a DHE for DMFC system are presented.

2. Experimental

2.1. Carbon activation using plasma—Ar–O_2 atmosphere

Carbon black (Vulcan XC72) was obtained from Cabot Carbon Corporation. Plasma treatment process for the carbon black was carried out using plasma treatment device, as shown in Fig. 1 (Institut für Niedertemperatur-Plasmaphysik e.V., Greifswald, Germany). The operation conditions were: 27.12 MHz frequency, 150 W power, 20 min residence time, Ar–O_2 atmosphere, and 20 mbar gas flow at room temperature.

2.2. Electrocatalysts preparation

The electrocatalysts, with 30% of PtRu in carbon black, were prepared using the impregnation-reduction method and direct reduction with hydrazine. In the procedure, 200 mL of N_2H_2 were added to 2 g of carbon black (Vulcan XC72, Cabot Co.). 1.5 g of
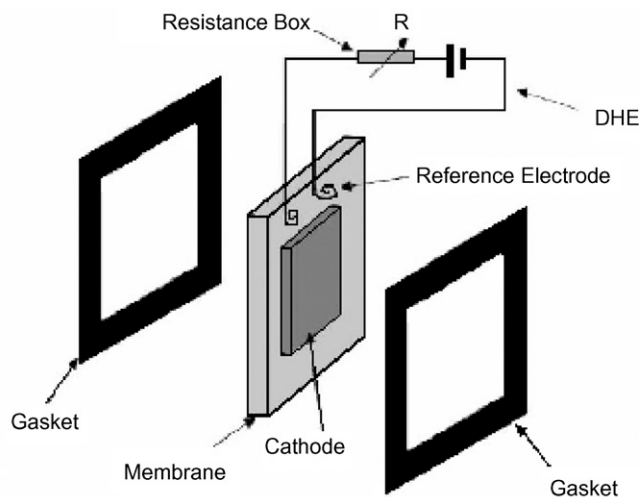

Fig. 2. Model of the DHE technique applied in the MEA with plasma carbon black activation.

RuCl$_3$ was dissolved in 400 mL of 2-ethoxy-ethanol and 1.5 g of H$_2$PtCl$_6$ was dissolved in 200 mL of ethylene glycol. The reagents were mixed together and ultrasonically dispersed for 15 min. After that, they were refluxed, stirred and heated for 15 min. The resulting powder (PtRu/C 30%) was filtered, washed with Milli-Q water and dried overnight.

2.3. Physical characterization

The PtRu atomic ratios of the electrocatalysts were obtained by using a Philips XL30 scanning electron microscope coupled to an EDAX DX-4 microanalyzer with a 20-keV electron beam.

The transmission electron microscopy (TEM) characterization was done using a JEOL JEM-1200EX microscope, and the average particle size was calculated using the Image Tool Software with one TEM micrograph for each catalyst.

2.4. Electrochemical characterization

2.4.1. DMFC characterization

To prepare the MEA's, water and a desired amount of the conducting polymer dispersion (Nafion®) were added to the catalyst powder. The system was mixed with a ultra-turrax system for 10 min and stirred at 90 °C, until the loss of water was sufficient, resulting in an optimum paste to be applied by the screen printing technique. The amount of catalytic material (metal loading) was controlled after the printing process. After screen printing, heat treatment was carried out at 135 °C for 30 min [28,29]. The membrane was treated with nitric acid 5 wt.% at 100 °C and than washed in hot Milli-Q water followed by cold Milli-Q water. The MEA were placed in the single cell, using for the anode Toray paper (TGP-H-060) and for the cathode Sigracet 10CC from SGL as gas diffusion layer (GDL), respectively. The operation
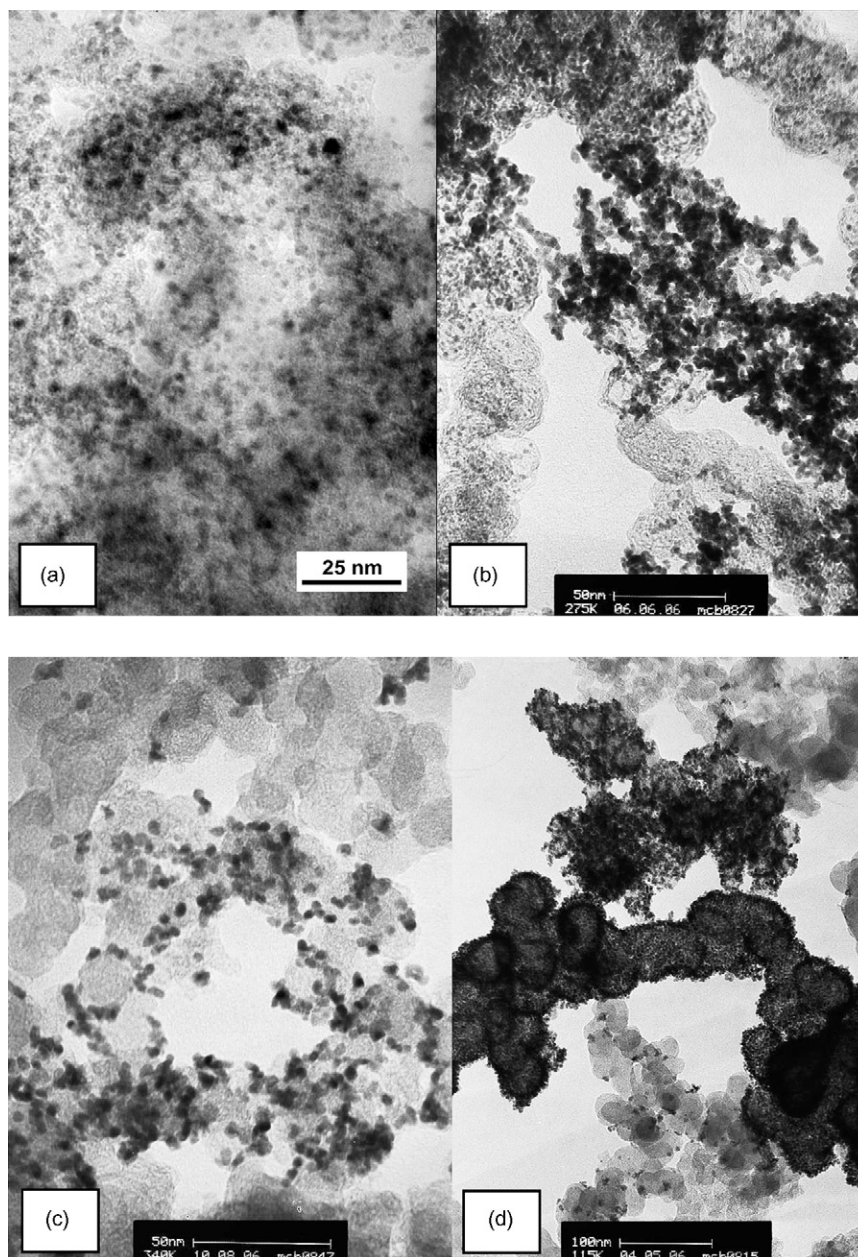
Fig. 3. TEM micrographs for (a) PtRu/C E-TEK commercial catalyst, (b) PtRu/C HISPEC commercial catalyst, (c) PtRu/C catalyst (carbon non-functionalized) and (d) PtRu/C-Plasma catalyst.

was started at 200 mV for DMFC, and after this time, the polarization curve was recorded. The experimental conditions for DMFC were: single test cell HIAT FC25/125, contact pressure on electrochemical active area of 1 N mm^{-2}, air flow of 1.5 N L min^{-1} (100% humidity), CH_3OH 3.5% flow of 15 mL min^{-1}. The applied cell temperature was 70 °C. The gas diffusion layers used were; anode: 0.6 mg$_{PtRu}$cm^{-2} with a Toray paper TGP-H-060 and cathode: 1.5 mg$_{Pt}$ cm^{-2} with a Toray paper Sigracet 10CC. The electrolytic membrane was Nafion® 117.

2.4.2. DHE characterization

Fig. 2 shows a schematic diagram of the edge-type DHE reference electrode configuration used in this work. The working electrode and counter electrode of the DHE were 0.1 mm diameter Pt wires placed on the anode side of an outer section of the Nafion® membrane and sandwiched between the two halves of the body of the cell. The distance between the ends of the Pt wires and the edge of active electrodes of the fuel cell was always much larger than three times the thickness of the membrane to avoid potential gradients. A constant current of ca. 6 μA to operate the DHE was fed by a series connection of a dry battery (9 V) and an adjustable resistor (0–1 MΩ) adjusted beforehand, as a floating current source having no interference with other instruments. This current was allowed to pass between the two Pt wires to maintain the hydrogen coverage on the cathode, which was used as the DHE. Except at the two ends, the Pt wires were insulated with a thin coating of poly(vinyl chloride). Before measurements, the fuel cell was fed with hydrogen on the anode and the potential of the reference electrode was set to zero with respect to the hydrogen anode by changing the series resistance. In order to check the stability of the DHE reference electrode during operation of the fuel cell, its potential was periodically measured with respect to the open circuit potential of the fuel cell anode, which acts as a reversible hydrogen electrode (RHE). The cell voltage and over-potentials of anode and cathode were measured and recorded from the open circuit voltage to short circuit.

3. Results and discussion

3.1. Energy dispersive X-ray analysis (EDX)

EDX analysis showed no, or at least only small, discrepancies compared with the nominal compositions used to calculate the precursor's quantities in the catalysts preparation. The results showed that the method used to prepare the electrocatalytic systems was very suitable.

3.2. Transmission electron microscopy

The TEM images are presented in Fig. 3, the TEM particle size histograms are given in Fig. 4. These results reveal a very homogenous and uniform particle distribution on the support surface for the material PtRu/C ETEK and less homogeneous for the PtRu/C HiSPEC of Johnson Matthey. However, for the PtRu/C catalyst without and with plasma activation, some substantial differences related to the others were noted. The two materials present the same non-homogeneous surface and non-uniform particle distribution with a lot of agglomerates. But despite of this, the material with plasma treatment presented a beneficial reduction in the particle size, about 3.2 nm compared with the material without treatment (4.7 nm). Looking at the histograms, the electrocatalyst supported on carbon with plasma treatment presents a narrower particle size distribution. Another very important result is that the commercial material has a particle size distribution in the average range of 2–4 nm, which only corresponds to 60% of these particles; however, the material with
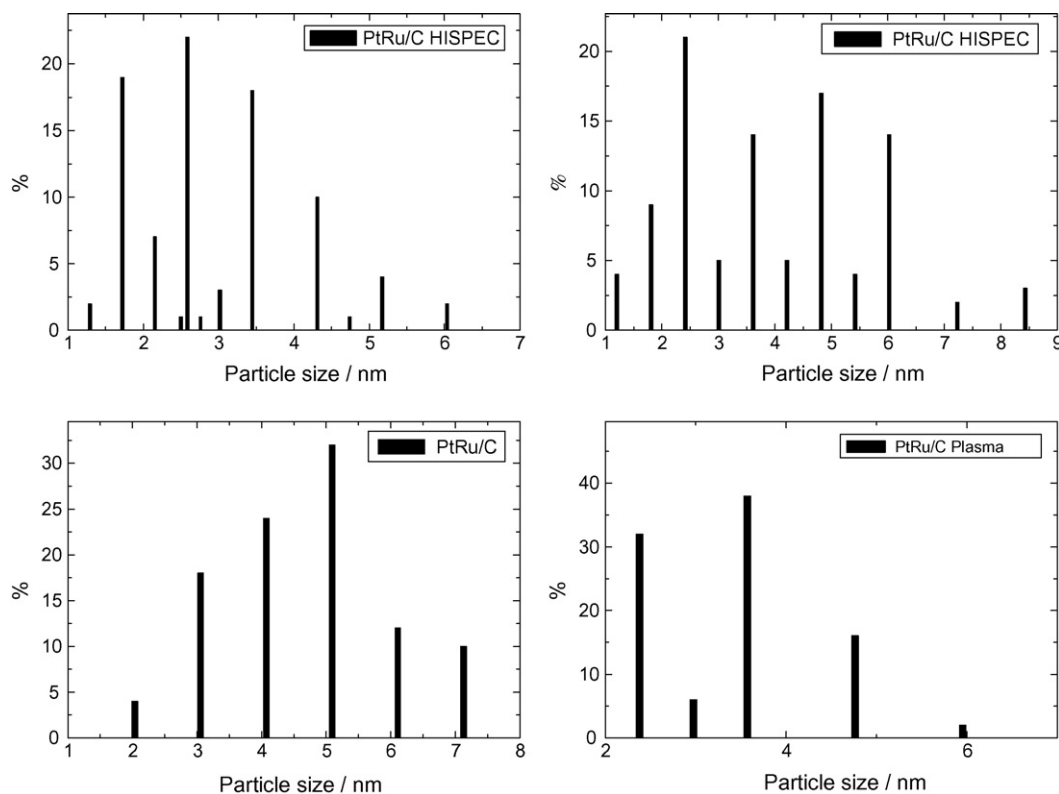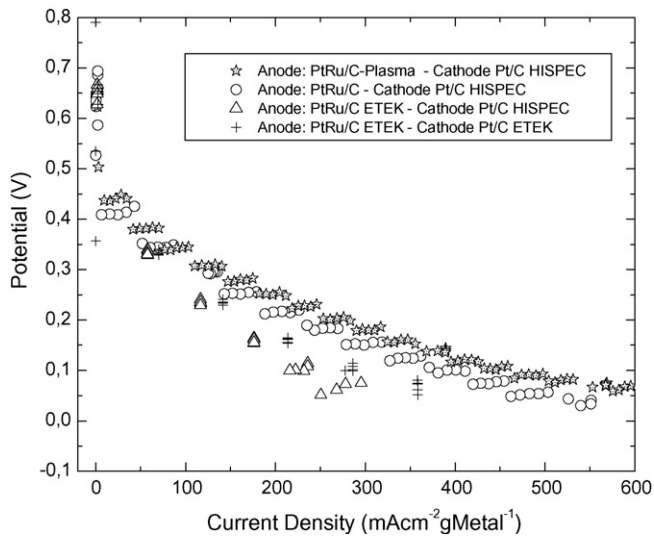

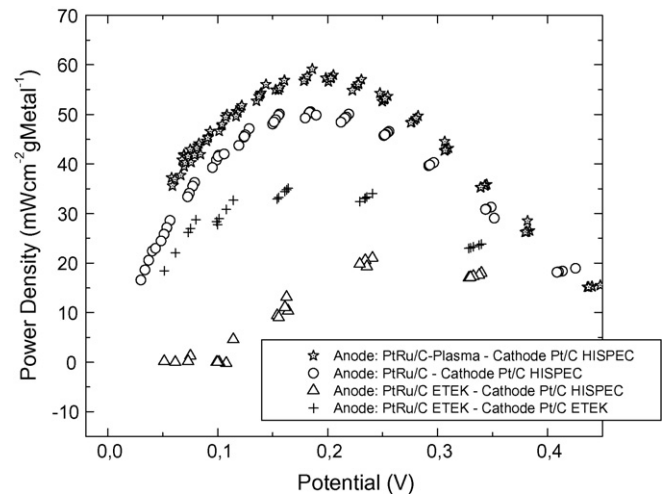**Fig. 4.** Particles size histograms for the prepared materials obtained with TEM analysis.

Fig. 5. Polarization curves, working with methanol/air, operational conditions—test cell: HIAT FC25/125, cell torch: 1 N mm^{-2}, air: 1.5 N L min^{-1} (100% humidity), CH$_3$OH 3.5%: 15 mL min^{-1}, cell temperature 70 °C, GDLs: anode Toray, cathode SGL 10CC.

Fig. 6. Power density vs. potential curves, working with methanol/air, operational conditions—test cell: HIAT FC25/125, cell torch: 1 N mm^{-2}, air: 1.5 N L min^{-1} (100% humidity), CH$_3$OH 3.5%: 15 mL min^{-1}, cell temperature 70 °C, GDLs: anode Toray, cathode SGL 10CC.

plasma treatment has about 75% of its particles with average sizes of 2–4 nm. Plasma treatment leads to a high and homogenous activation of the carbon support with oxygen groups, which are necessary for the homogenous deposition of catalysts.

3.3. Fuel cell tests

The DMFC polarization curves and power density curves for PtRu/C-Plasma and PtRu/C ETEK (with ETEK or HiSPEC cathode) working with methanol at approx. 1.1 mol L^{-1} (3.5 wt%) and air are presented in Figs. 5 and 6 The cathode was set as standard, using commercials materials as Pt/C HiSPEC and Pt/C E-TEK.

The PtRu/C-Plasma treated catalyst realized a maximum power density of 60 mW cm^{-2} g$_{metal}^{-1}$, the PtRu/C catalyst without treatment: 50 mW cm^{-2} g$_{metal}^{-1}$, PtRu/C E-TEK: 35 mW cm^{-2} g$_{metal}^{-1}$ and PtRu/C E-TEK with the HiSPEC cathode: 16 mW cm^{-2} g$_{metal}^{-1}$. The performance of the plasma treated material was at least 20% better compared to the non-treated material, and 71% better compared to commercial materials. Looking at the polarization curve in Fig. 5, the plasma treated electrode shows a better polarization curve behavior in the region dominated by mass

transfer. A reason for this can be the better penetration of the electrode with fuel compared to other non-treated materials. Probably the plasma "cleans" the surface of the carbon support, too.

Summarizing, the results presented the following performance order: PtRu/C-Plasma > PtRu/C > PtRu/C ETEK with ETEK cathode > PtRu/C ETEK with HISPEC cathode.

3.3.1. PtRu/C-Plasma activated DHE fuel cell tests

It is usual in DMFC R&D to get "anode polarization" curves by feeding the fuel cell cathode with hydrogen and assuming that it behaves as a reversible hydrogen electrode [27–29]. The data obtained in this way should approximate the behavior of the anode in the operating fuel cell (with air or O$_2$ on the cathode), which can be measured with the use of a reference electrode. However, the innovative DHE provides more accurate and reliable anode polarization results than the use of a RHE cathode, since hydrogen passing through the cathode could significantly perturb the behavior of the methanol anode, while the use of a DHE allows the real anode performance to be evaluated in the DMFC with air or oxygen on the cathode [23].
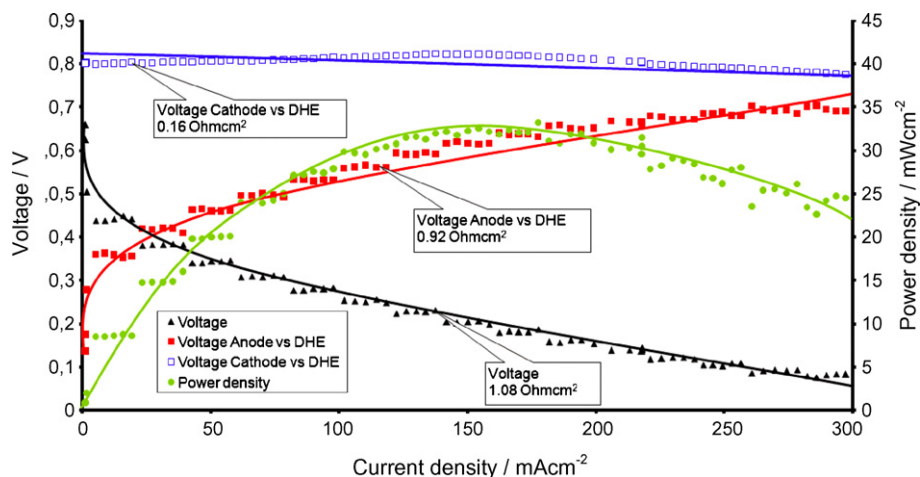
Fig. 7. Anode potential vs. DHE and cathode potential vs. DHE for the PtRu/C material with plasma activation.

When the PEMFC was operated at fixed currents in the range of 0 (open circuit) to 500 mA cm^{-2}. At any current density, fluctuations of several millivolts were observed. In any case, the magnitude of the fluctuations is ca. 5 mV, and the stability of the DHE is within this range.

A possible explanation for the fluctuations with time of the DHE potential have been already proposed [20]. It was discussed that the partial pressure of hydrogen gas in contact with the hydrogen evolution wire exceeds the environmental pressure and is not stable.

Fig. 7 shows the cell voltage and the separated anode and cathode PtRu/C-Plasma polarization curves for a DMFC set with an edge-type DHE. The differences noted are mainly due to variations in the operation of the cell from one experiment to another. The anode and cathode polarization curves are similar to others in literature [21–27]. They show that there is a substantial anode overpotential, even at low current densities, and that the cathode potential is decreased greatly at low current densities by methanol crossover. The cathode overpotential decreased at high current densities, but not significantly, indicative of a good water removal, water that was produced by the cathode reaction.

4. Conclusions

The impregnation method—hydrazine reduction was suitable for catalysts preparation. The energy dispersive analysis (EDX) results of the catalysts are in good agreement with the method utilized, showing that the method was successful in producing catalysts with the desired compositions. TEM particle size results showed a beneficial decrease in the particle average size for the plasma treated material compared with the material without treatment, but with a less homogeneous particle size distribution. For DMFC operation, using the PtRu/C-Plasma material, it was obtained a power density of 60 mW cm^{-2} g$_{metal}^{-1}$, and compared with the PtRu/C ETEK commercial material, 35 mW cm^{-2} g$_{metal}^{-1}$, the performance was at least 42% better. Summarizing, the DMFC performance order, regarding the catalyst system used was PtRu/C-Plasma > PtRu/C > PtRu/C ETEK with ETEK cathode > PtRu/C ETEK, with HiSPEC cathode. The DHE device proved to be a suitable and efficient tool to evaluate the anode and cathode DMFC performance, providing important observations for each electrode of the cell.

References

[1] H. Wendt, M. Gotz, M. Linardi, Quim. Nova 23 (4) (2000) 538–546.
[2] T. Frey, M. Linardi, Electrochim. Acta 50 (1) (2004) 99–105.
[3] F. Colmati, E. Antolini, E.R. Gonzalez, Electrochim. Acta 50 (28) (2005) 5496–5503.
[4] M. Carmo, V.A. Paganin, J.M. Rosolen, E.R. Gonzalez, J. Power Sources 142 (1–2) (2005) 169–176.
[5] E.I. Santiago, et al. J. Electroanal. Chem. 575 (1) (2005) 53–60.
[6] E. Spinace, A.O. Neto, M. Linardi, J. Power Sources 129 (2) (2004) 121–126.
[7] M. Mastragostino, A. Missiroli, F. Soavi, J. Electrochem. Soc. 151 (11) (2004) A1919–A1924.
[8] Z.B. Wang, G.P. Yin, P.F. Shi, Carbon 44 (1) (2006) 133–140.
[9] S. Biniak, G. Szymanski, J. Siedlewski, A. Swiatkowski, Carbon 35 (12) (1997) 1799–1810.
[10] B.K. Pradhan, N.K. Sandle, Carbon 37 (8) (1999) 1323–1332.
[11] F. Rodriguezreinoso, et al. Appl. Catal. 15 (2) (1985) 293–300.
[12] F. Rodriguezreinoso, et al. J. Catal. 99 (1) (1986) 171–183.
[13] S. Kim, M.H. Cho, J.R. Lee, S.J. Park, J. Power Sources 159 (1) (2006) 46–48.
[14] Y.H. Pai, et al. J. Power Sources 161 (1) (2006) 275–281.
[15] H. Shioyama, et al. J. Power Sources 161 (2) (2006) 836–838.
[16] Z.C. Tang, Q.Y. Li, G.X. Lu, Carbon 45 (1) (2007) 41–46.
[17] M. Carmo, A.R. Dos Santos, J.G.R. Poco, M. Linardi, J. Power Sources 173 (2007) 860–866.
[18] B. Ruffmann, B. Rohland, Chem. Ing. Tech. 77 (5) (2005) 539–548.
[19] B. Rohland, et al. Fullerenes Nanotubes Carbon Nanostruct. 13 (2005) 511–522.
[20] Z. Siroma, et al. J. Power Sources 156 (2) (2006) 284–287.
[21] B. Andreaus, A.J. Mcevoy, G.G. Scherer, Electrochim. Acta 47 (13–14) (2002) 2223–2229.
[22] S.H. Chan, X.J. Chen, K.A. Khor, J. Appl. Electrochem. 31 (10) (2001) 1163–1170.
[23] G.C. Li, P.G. Pickup, Electrochim. Acta 49 (24) (2004) 4119–4126.
[24] J. Winkler, P.V. Hendriksen, N. Bonanos, M. Mogensen, J. Electrochem. Soc. 145 (4) (1998) 1184–1192.
[25] S.B. Adler, et al. Solid State Ionics 134 (1–2) (2000) 35–42.
[26] A. Kuver, I. Vogel, W. Vielstich, J. Power Sources 52 (1) (1994) 77–80.
[27] X. Ren, T.E. Springer, S. Gottesfeld, J. Electrochem. Soc. 147 (1) (2000) 92–98.
[28] M.A. Short, P.L. Walker, Carbon 1 (1) (1963) 3–9.
[29] E.V. Spinace, M. Linardi, A.O. Neto, Electrochem. Commun. 7 (4) (2005) 365–369.