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RRDE study of oxygen reduction on Pt nanoparticles inside Nafion®: H_2O_2 production in PEMFC cathode conditions

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Abstract

Dihydrogen peroxide production on platinum particles supported on carbon inside a proton exchange membrane (Nafion®), that is, under the working conditions of PEMFC cathodes, is rather small at the usual oxygen reduction potentials. As on bulk platinum, a four-electron mechanism appears to be the main pathway, with particle size and carbon substrate effects on the H_2O_2 production. A large increase in the H_2O_2 contribution takes place at low potentials, that is, at the working potentials of PEMFC anodes.

List of symbols

E_D	disc potential (V vs SCE)
d	diameter (nm)
I_D	disc current (A)
I_R	ring current (A)
I_{2e^-}	two-electron disc current (A)
I_{4e^-}	four-electron disc current (A)
$I_{2e^-}^{C\rightarrow Pt}$	2-electron reduction current of H_2O_2 (produced on C) by Pt particles in an active layer on the disc (A)
L	active layer thickness (μm)
N	collection efficiency of H_2O_2 produced on the disc and 'collected' on the ring
n_{e^-}	average number of exchanged electrons
%Pt/(Pt + C)	Pt mass ratio

1. Introduction

The oxygen reduction reaction (ORR) occurs as the cathodic process in numerous energy conversion processes. Therefore, this electrocatalytic reaction has been studied on numerous materials and electrolytes. The rotating ring-disc electrode (RRDE) methodology is commonly used for this study [1–9] since it enables the kinetics and the mechanism of the reaction to be determined. This method is able to quantitatively detect one possible intermediate species: dihydrogen peroxide (H_2O_2). The ORR takes place on the central disc electrode and the produced H_2O_2 is either oxidized or reduced on the concentric ring electrode, depending on the potential of this electrode. Several reaction mechanisms reviewed in [6] are proposed on bulk noble metals. They are analysed by Hsueh et al. [4] who define the Damjanovic mechanism [1] as the most realistic on platinum. The mechanism considers that the main reaction is the direct reduction of O_2 to H_2O (with a four-electron charge transfer), the rate determining step (rds) being O_2 protonation which takes place on bare platinum atoms. The secondary reaction is a parallel reduction to H_2O with an intermediate species: H_2O_2 in acidic media. RRDE studies for the ORR [3, 4] allow evaluation of the molar proportion of produced H_2O_2 on bulk platinum, either in aqueous sulphuric or phosphoric solutions.

The Damjanovic mechanism can be also assumed as valid on platinum nanoparticles in aqueous acidic solution; however no attempt has been made to perform a RRDE study on such particles. A particle size effect on ORR kinetics has been demonstrated [10–15]. The specific activity (SA) decreases with particles size, mainly below 2 nm, and there is a maximum mass activity (MA) between 3 and 4 nm in aqueous sulphuric and phosphoric acids. According to Kinoshita [10], this maximum corresponds to the optimum number of active surface atoms for cubo-octahedric platinum particles. Several studies [13–17] have demonstrated a correlation between the platinum particle size decrease and its increase in degree of surface oxidation for a

given potential (by degree of surface oxidation, we mean degree of surface coverage by intermediate oxygenated species). In accordance with the Damjanovic theory [18], this effect involves a current density decrease. There are very few papers on ORR on platinum particles in Nafion® [13, 14, 19]. From potentiostatic steady-state polarization curves and impedance measurements this mechanism was confirmed as the main reaction on Pt nanoparticles inside Nafion® [20]. But the platinum particle size and degree of surface coverage by intermediate oxygenated species could also influence the secondary reaction of H_2O_2 production. In this paper, an experimental RRDE study of ORR on platinum nanoparticles supported on carbon (in a Pt/C + Nafion® active layer) is proposed in order to clarify the particle size and carbon substrate effects on H_2O_2 production.

2. Experimental details

A glass cell was used. The reference electrodes were two saturated calomel electrodes (SCE), each immersed in an isolated compartment connected to the cell by a Luggin–Haber capillary. These ionic bridges avoid electrolyte contamination by chlorides. Two platinum grids were used as counter electrodes for disc and ring electrodes. The [glassy carbon disc-bulk platinum ring] Pine Instrument electrode (AFDT21 [21]) was used as working electrodes. Disc and ring electrode potentials were respectively controlled by EGG PAR and Tacussel potentiostats and measured versus the SCE reference electrodes. The rotation rate was controlled by a Pine Instrument system (AFASRE [21]). The disc and ring currents were recorded as a function of disc potential on an Ifélec X double Y_1Y_2 paper recorder. The working ring-disc electrode was polished using 1 μm diamond paste and then cleaned in acetone, ethanol and very pure water (see below). The disc electrode was coated with an active layer [22] made of Nafion® and E-TEK® platinum nanoparticles supported on carbon (Vulcan XC-72 from Cabot) [23]. The Pt/C, Nafion® solution was sonicated, dropped on the disc with a microsyringe and dried at room temperature.

The geometric characteristics of the RRDE allow calculation of the theoretical collection efficiency (disc radius 2.50 mm, ring inner radius 2.76 mm, ring outer radius 3.58 mm, $N_{th} = 0.394$ [21]). The ring/disc current ratio allows calculation of the experimental collection efficiency. $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ redox couple is generally used to determine the collection efficiency value up to 10,000 rpm, but cannot be used with a cation exchange membrane (Nafion®) on the disc active layer. In this case, Fe^{3+}/Fe^{2+} redox couple with 1 M H_2SO_4 was used, but only up to 3200 rpm, to avoid the bond separation of the active layer. The difference between the theoretical collection efficiency ($N_{th} = 0.394$) [21] and the experimental one does not exceed 5% and is probably due to the micrometric active layer thickness.

A 0.1 M electrolyte was prepared from Merck suprapur concentrated sulphuric acid diluted with ultrapure water (Millipore SuperQ System, resistivity: 18 MΩ cm). Cyclic voltammograms (10 mV s^{-1}) were recorded under high purity argon gas to verify the electrode and electrolyte cleanliness (no change with cycle number or rotation rate), and to determine the electrochemically-active platinum surface area from hydrogen adsorption–desorption coulometry.

Before the RRDE experiments were performed, the electrolyte was saturated with 99.999 pure oxygen for 10 min. The disc electrode potential was then scanned between 0.7 V vs SCE and 0 V vs SCE (or −0.3 V vs SCE) at 1 mV s^{-1}, the ring electrode potential being held at 1 V vs SCE in order to obtain the oxidation limiting current of H_2O_2 into O_2. This experiment was performed at 293 K for a series of rotation rates (ω). The rotation rate influence on the collection efficiency (N) and the average number of exchanged electron (n_{e^-}) is very small. Therefore, only one rotation rate is reported in this paper ($\omega = 800$ rpm).

The disc and ring currents (I_D and I_R, respectively) were recorded as a function of the disc electrode potential E_D. The average number of exchanged electrons (4) during the reduction of one molecule of O_2 was calculated from the charge (1, 2) and mass (3) balance equations. The two- and four-electron disc currents are $I_{2e^-}(\rightarrow H_2O_2)$ and $I_{4e^-}(\rightarrow H_2O)$, respectively. The current related to the series reaction pathway ($O_2 \rightarrow H_2O_2 \rightarrow H_2O$) is assumed to be negligible, or included in the four-electron disc current:

$$I_{2e^-} = I_R/N \tag{1}$$

$$I_D = I_{2e^-} + I_{4e^-} \tag{2}$$

$$\frac{I_D}{n_{e^-}} = \frac{I_{4e^-}}{4} + \frac{I_{2e^-}}{2} \tag{3}$$

Thus,

$$n_{e^-} = \left(\frac{4I_D}{I_D + I_R/N}\right) \tag{4}$$

The H_2O_2 electronic proportion I_R/NI_D can be expressed as

$$\frac{I_R}{NI_D} = \frac{4}{n_{e^-}} - 1 \tag{5}$$

Therefore, the H_2O_2 molar proportion $(I_{2e^-}/2)/(I_D/n_{e^-})$ is

$$\frac{I_{2e^-}/2}{I_D/n_{e^-}} = \frac{4 - n_{e^-}}{2} \tag{6}$$

The H_2O_2 electronic and molar proportions decrease when the average number of exchanged electrons increases. A factor 2 between these two proportions is

found when n_{e^-} approaches 4. The accuracy of Equations 4 and 5, and therefore 6, depend mainly on the accuracy of the experimental measurement of the collection efficiency, of which the error is very small (<1%). However, the possible error increases when very low ring current values (i.e., n_{e^-} close to 4) are measured.

3. Results and discussion

The size and platinum surface area of E-TEK® particles decrease when the platinum mass ratio diminishes: 10% Pt/(Pt + C), $d = 2.5$ nm; 20%, 3.4 nm; 30%, 4.1 nm; 40%, 5.1 nm [13, 22, 23]. The ORR disc current is related to the geometric area (Figure 1(a)) and increases when the platinum mass ratio, and hence the particle size, increases. On the other hand, the H_2O_2 oxidation ring current (Figure 1(b)) decreases when the platinum particle size increases.

Figure 2 shows the average number of exchanged electrons as a function of the disc potential. There is a minimum around 0.5 V vs SCE for all platinum particle sizes, and a continuous decrease for lower potentials. The H_2O_2 proportion increases when the disc potential decreases: H_2O_2 production increase is probably due to O_2 reduction on carbon, which only occurs at low potentials (high overpotentials). There is also a particle size effect on the average number of exchanged electrons. The average number decreases, and the H_2O_2 proportion increases, when the particle size decreases, but this H_2O_2 proportion is small: <0.75% and <1.5% for 0.5 and 0 V vs SCE, respectively, for the smallest particles (10% Pt/(Pt + C), d = 2.5 nm). These low H_2O_2 proportions on platinum particles are similar to those on bulk platinum [4, 5]. The I_D/I_R vs $\omega^{-1/2}$ relationships [6] allow us to study the order of the reaction with respect to O_2, and the values of the constant rates of the four- and two-electron reactions. As found by Srinivasan et al. [4] on bulk platinum, we can also show that the reaction is first order with respect to O_2 and that the four-electron direct reaction [20] is very fast. Therefore, we assume a Damjanovic mechanism for the ORR on platinum nanoparticles.

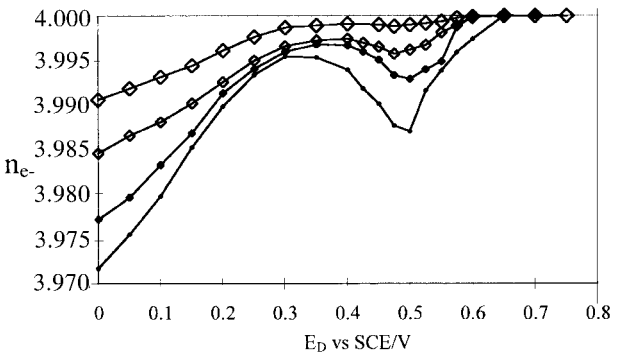

Fig. 2. Average number of exchanged electrons $n_{e^-} = F(E_D)$ during oxygen reduction on the disc active layer (same conditions as in Figure 1).

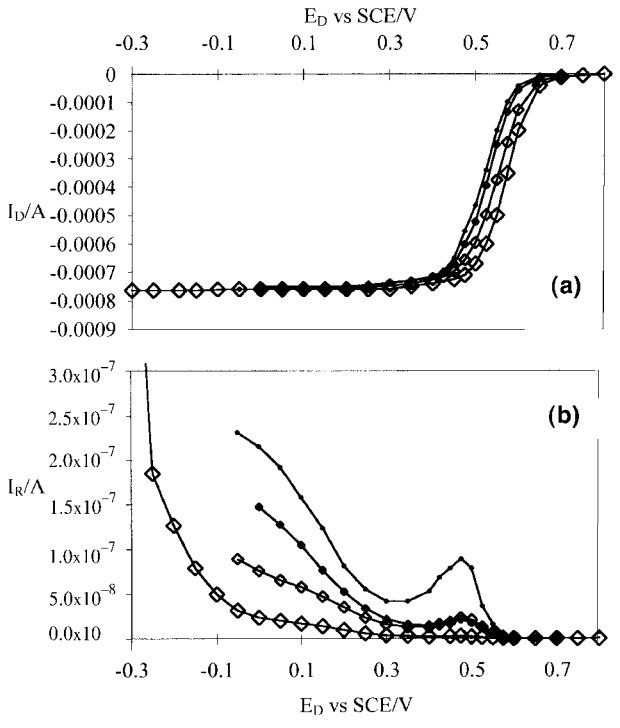

Fig. 1. Oxygen reduction curves (a) on the disc electrode $I_D = F(E_D)$ for active layers with different platinum mass ratios Pt/(Pt + C), and dihydrogen peroxide oxidation curves (b) on the ring electrode $I_R = F(E_D)$ (1 mV s^{-1}; 0.1 M H_2SO_4; 293 K; $L \approx 3\,\mu$m; Nafion®/carbon volume ratio = 1; 10% Pt/(Pt + C): (◇) $d = 2.5$ nm, $S_{Pt} = 7.6\,cm^2$; 20%: (◇) $d = 3.4$, $S_{Pt} = 13.9\,cm^2$; 30%: (◇) $d = 4.1$, $S_{Pt} = 19.4\,cm^2$; 40%: (◇) $d = 5.1$, $S_{Pt} = 24.3\,cm^2$).

According to our studies [13, 14] and those of Boudart et al. [16] and Hwang et al. [17], the degree of particle surface coverage by intermediate oxygenated species is larger for the smallest particles sizes. This higher coverage could be correlated with the larger proportion of low coordination surface atoms (tops and edges). This higher coverage was also assumed to be responsible for the particle size effect on the ORR (cf. Damjanovic mechanism: r.d.s. on bare platinum). We also suggest that the four-electron ORR process requires bare platinum atoms for the bridged side-on O_2 adsorption (for dissociative adsorption). When the degree of particle surface coverage by intermediate oxygenated species increases, the area of bare platinum surface for bridged side-on O_2 adsorption is limited. Thus, we assume an increase in the bridged end-on O_2 adsorption and of H_2O_2 production as this mode of adsorption is not dissociative [2, 5].

The carbon substrate probably has an influence on H_2O_2 production. The carbon/platinum surface area ratio increases strongly when the particle size decreases, especially below 5 nm (Figure 3). Therefore, the carbon substrate influence is assumed to be stronger for the smallest particle sizes.

The H_2O_2 proportion in an active layer, with and without platinum nanoparticles, was studied in order to elucidate the carbon substrate influence. The carbon substrate (Vulcan XC-72 from Cabot) was activated at

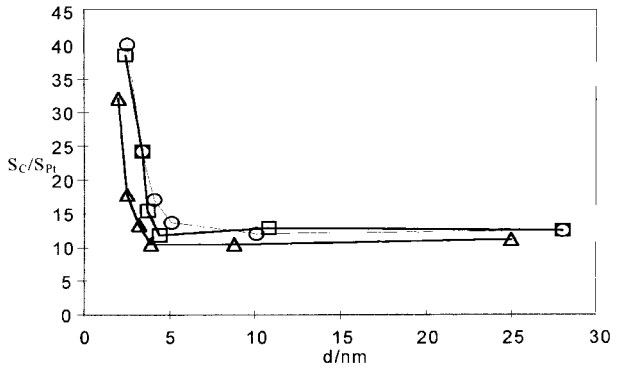

Fig. 3. Carbon surface area to platinum surface area ratio as a function of the platinum nanoparticle size calculated from TEM observations and cyclic voltammograms results under argon gas (□) [13], carbon monoxide gas (○) [13] and from E-TEK® data (△) [23].

1203 K under CO_2 for 1 h. The active layer without platinum nanoparticles is a mixture of this activated carbon and Nafion® (volume ratio equal to 1). In this case, given our previous assumptions, the four- and two-electron currents on carbon ($I^C_{4e^-}$ and $I^C_{2e^-}$, respectively) can be calculated from the disc and ring currents (I^C_D and I^C_R, respectively) (1′, 2′) [24]:

$$I^C_R/N = I^C_{2e^-} \quad (1')$$

$$I^C_D = I^C_{4e^-} + I^C_{2e^-} \quad (2')$$

The active layer with platinum is a mixture of Nafion® and H_2PtCl_6 impregnated on carbon (i.e., 10% Pt/(Pt + C)), prepared with the same amount of activated carbon. The electrochemical reduction leads to platinum nanoparticles on carbon which are homogeneous in size and separation [25, 26]. Their sizes were checked by TEM and cyclic voltammograms under argon gas, and were found to be around 3 nm. In this case, the four- and two-electron currents on carbon ($I^C_{4e^-}$ and $I^C_{2e^-}$ respectively), already known from (1′, 2′) and on platinum particles ($I^{Pt}_{4e^-}$ and $I^{Pt}_{2e^-}$ respectively) are involved in the disc and ring currents ($I^{Pt/C}_D$ and $I^{Pt/C}_R$, respectively) (7, 8). However, there is another unknown current ($I^{C\to Pt}_{2e^-}$) which is related to the electrochemical reduction of H_2O_2, produced on the carbon, by the platinum particles. The current intensity balance on the disc must involve the addition of this current ($I^{C\to Pt}_{2e^-}$), and that of carbon alone ($I^C_{2e^-}$). Considering the reoxidation of H_2O_2 on the ring, the ($I^{C\to Pt}_{2e^-}$) current must be subtracted (and it is far from negligible, see Figure 4) from the current intensity balance on the ring.

$$I^{Pt/C}_D = I^{Pt}_{4e^-} + I^C_{4e^-} + I^{Pt}_{2e^-} + I^C_{2e^-} + I^{C\to Pt}_{2e^-} \quad (7)$$

$$I^{Pt/C}_R/N = I^{Pt}_{2e^-} + I^C_{2e^-} - I^{C\to Pt}_{2e^-} \quad (8)$$

There are two equations (7, 8) and three unknown currents ($I^{Pt}_{4e^-}$, $I^{Pt}_{2e^-}$, $I^{C\to Pt}_{2e^-}$). Therefore, there is an indetermination. Modelling in progress at present, has

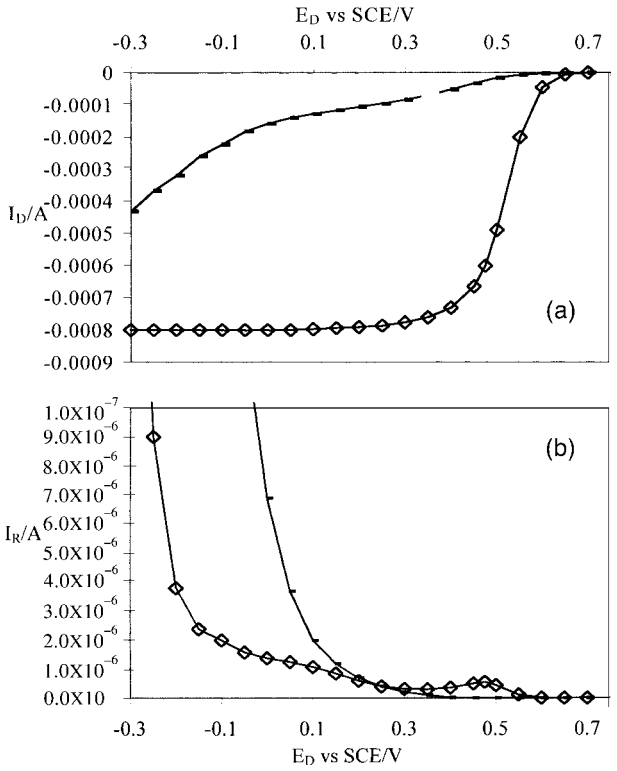

Fig. 4. Oxygen reduction curves (a) on the disc electrode $I_D = F(E_D)$ for two active layers with carbon alone (—) or with carbon with platinum nanoparticles (◇), and dihydrogen peroxide oxidation curves (b) on the ring electrode $I_R = F(E_D)$(1 mV s^{-1}; 0.1 M H_2SO_4; 293 K; $L \approx 3\,\mu$m; Nafion®/carbon ratio = 1; Vulcan XC72R alone or with a 10% Pt/(Pt + C) [25, 26]).

to consider the active layer geometry, the diffusion coefficients and solubility values in the layer, and three reduction kinetics on the Pt particles (in fact three unknown functions). This demonstrates the necessity to add experiments which involve H_2O_2 in solution (instead of O_2), and some with mixtures of H_2O_2 and O_2. Our case is more complex than the recently-considered case of a Nafion® layer on the bulk metal disc of a RRDE [27]. Moreover, we did not considered the dismutation of H_2O_2 on Pt particles inside the active layer, which gives 0.5 molecule of O_2 for every initial O_2 molecule, and would take place in a pathway not easily separable from a direct four-electron reduction. This dismutation reaction, important in alkaline media, is generally neglected in acidic ones [4]. At present, we can only compare the disc and ring currents for the two active layers in various potential regions.

For all potentials, the ORR disc current on carbon is smaller than the ORR current on carbon and platinum particles (Figure 4(a)). On the other hand, below 0.3 V vs SCE, the oxidation ring current of H_2O_2 (produced on carbon alone) is stronger than the oxidation ring current of H_2O_2 (produced on carbon and platinum particles) (Figure 4(b)).

Figure 5 shows the average number of exchanged electrons as a function of the disc potential, for both carbon and platinum particles and for carbon alone. Above 0.4 V vs SCE, the H_2O_2 proportion on carbon

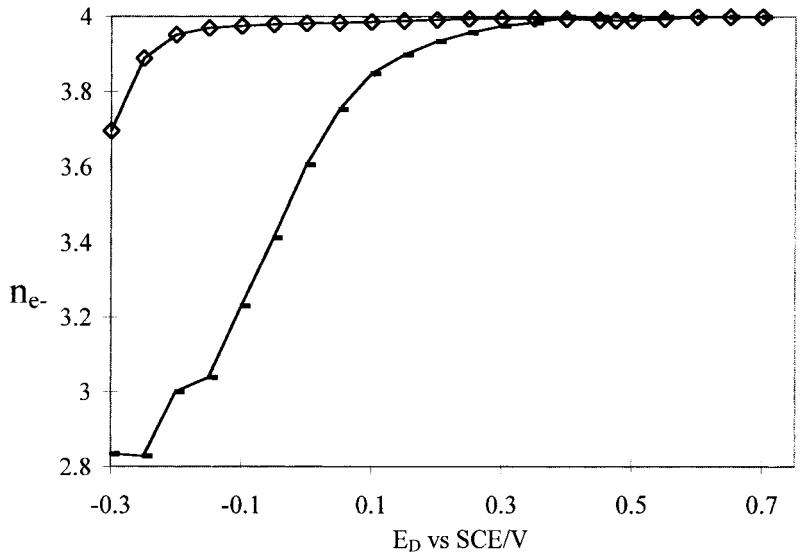

Fig. 5. Average number of exchanged electrons $n_{e^-} = F(E_D)$ during oxygen reduction on the disc active layer (same conditions as in Figure 4).

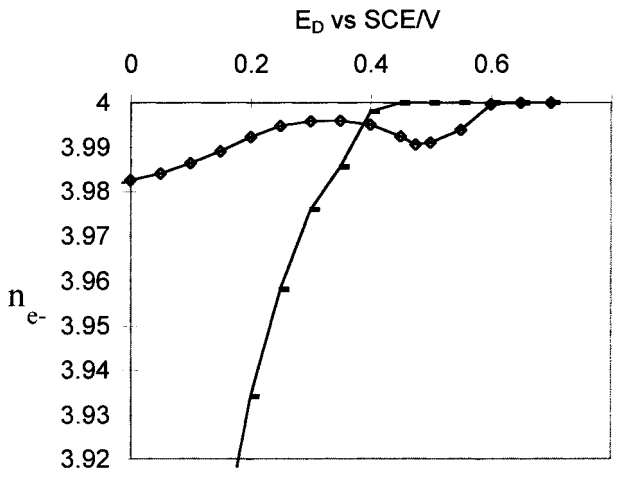

Fig. 6. Extending of the Figure 5.

alone is negligible and the H_2O_2 proportion on carbon and platinum particles is small: ~0% and <0.5% (around 0.5 V vs SCE). Therefore, carbon is not responsible for the weak particle size effect on the H_2O_2 production above 0.4 V vs SCE. Below 0.4 V vs SCE, the H_2O_2 proportion on carbon alone is stronger than the H_2O_2 proportion on carbon and platinum particles: <20% and <1% (around 0 V vs SCE) respectively. Therefore, the H_2O_2 which is produced on carbon is mainly reduced, or destroyed by dismutation, into H_2O on platinum particles.

The molar proportions of H_2O_2 produced on carbon alone and on carbon and platinum particles are strong for low potentials: ~58% and ~15%, respectively (at −0.3 V vs SCE, i.e. ~0 V vs RHE). This H_2O_2 production might be significant for PEMFC since the O_2 quantity which diffuses from the cathodic active layer across the Nafion® membrane towards the anode is not negligible. O_2 is then either electrochemically reduced into H_2O and H_2O_2 or catalytically recombined with hydrogen to give H_2O.

4. Conclusion

This RRDE study shows a weak platinum particle size effect on H_2O_2 production during the ORR. The H_2O_2 proportion increases when the platinum particle size decreases. Nevertheless, the molar proportion does not exceed 1% and it is suggested that a direct four-electron transfer is the main ORR mechanism on platinum nanoparticles in proton exchange membranes.

Above 0.4 V vs SCE, H_2O_2 is only produced on platinum nanoparticles. However, below 0.4 V vs SCE, H_2O_2 is mainly produced on carbon, and to a large extent reduced on platinum nanoparticles. Finally, a rather large H_2O_2 production is obtained at H_2/O_2 PEMFC anode potentials under the conditions of RRDE.

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