



Short communication

## Hexadecacarbonylhexarhodium as a novel electrocatalyst for oxygen reduction and hydrogen oxidation in the presence of fuel cell contaminants

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## ABSTRACT

The electrocatalytic activity for oxygen reduction and hydrogen oxidation of a discrete metal carbonyl cluster with a well defined molecular and crystal structure, Rh<sub>6</sub>(CO)<sub>16</sub>, is reported. The exchange current density of this compound for oxygen reduction is one order of magnitude higher than that of platinum, and its resistance degree to PEM fuel cell contaminants such as methanol and CO is as high as 2 mol L<sup>-1</sup> and 0.5%, respectively. These properties make the metal complex a potential alternative for use as electrode in polymer electrolyte membrane fuel cells.

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## 1. Introduction

The electrocatalysts for the oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR) in acid media, of which platinum is the primary metal employed, exhibit various technical problems, such as a severe performance decrease or even deactivation by species like methanol and CO. Such two reactions are the basic processes for the production of energy in fuel cells, and hence the importance of searching for novel, highly effective and contaminant tolerant electrocatalysts [1–4]. Most of the alternative catalysts known to date are basically metal nanoparticles or materials with composition and/or structure yet to be defined [5–9]; a few transition metal complexes with nitrogen macrocyclic ligands have been reported as well [10,11]. In this work, we report the electrocatalytic activity of a stable, discrete molecular compound, Rh<sub>6</sub>(CO)<sub>16</sub>, for the ORR and HOR, even in the presence of common contaminants of PEM fuel cell electrodes, such as CO and methanol. The crystal and molecular structure of this compound have been well characterized too [12,13]. Its catalytic properties for some organic reactions are well known [14], however, its potential as electrocatalyst for both the ORR and HOR – a *dual* behavior – have not been demonstrated before.

## 2. Experimental

Hexadecacarbonylhexarhodium [Rh<sub>6</sub>(CO)<sub>16</sub>] was purchased from Sigma–Aldrich and used as received. The rotating disk electrode (RDE) measurements were performed using a common electrochemical cell. A mercury sulfate electrode (Hg|Hg<sub>2</sub>SO<sub>4</sub>|0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>||) and a carbon cloth were used as reference and counter electrode, respectively. A Radiometer Analytical BM-EDI101 glassy carbon RDE (with a CTV101 speed control unit) was used as working electrode. The 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> electrolyte was prepared with 98% sulfuric acid (J. T. Baker) and deionized water. A PAR 263-A potentiostat/galvanostat was used for the electrochemical measurements.

An ink-type electrode was prepared with 0.5 mg of Rh<sub>6</sub>(CO)<sub>16</sub>, 2.5 mg of carbon powder (Vulcan<sup>®</sup> XC72R; Cabot) and 20 μL of a 5% Nafion<sup>®</sup> solution (ElectroChem) mixed in an ultrasonic bath; 3 μL of the resulting slurry were deposited on the RDE surface and dried in air. The geometrical area of the electrode was 0.072 cm<sup>2</sup>. Cyclic voltammetry (CV) experiments were done at a 20 mV s<sup>-1</sup> rate, in the absence and presence of methanol (1.0 and 2.0 mol L<sup>-1</sup>) and carbon monoxide (100 ppm and 0.5%, v/v in H<sub>2</sub>). Linear sweep voltammetry (LSV) was used for the ORR and HOR studies. Current–potential curves were obtained in the E<sub>02</sub><sup>O</sup> to 0.1 V/NHE and E<sub>0c</sub><sup>H</sup> to 0.4 V/NHE range, respectively, at 5 mV s<sup>-1</sup>. The rotation rates ranged from 100 to 900 rpm. The measurements were also performed in the presence of methanol and carbon monoxide for the ORR and HOR, respectively.

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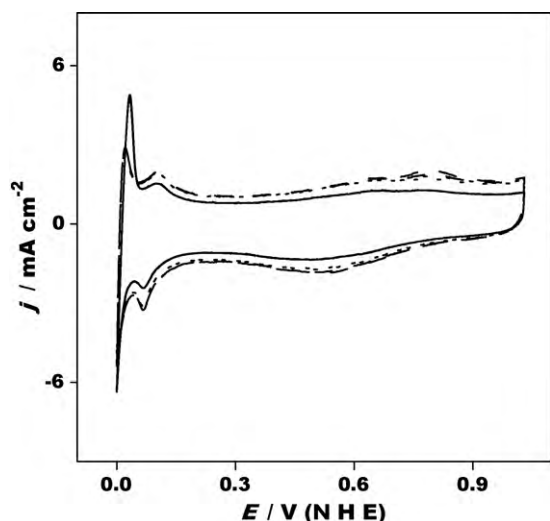


Fig. 1. Cyclic voltammograms of Rh<sub>6</sub>(CO)<sub>16</sub>/Vulcan® without methanol or CO (-); with 2.0 mol L<sup>-1</sup> methanol (- -); and with 0.5% carbon monoxide *in situ* (.....).

### 3. Results and discussion

Fig. 1 shows cyclic voltammograms of Rh<sub>6</sub>(CO)<sub>16</sub>/Vulcan® in N<sub>2</sub> saturated 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, in the absence and presence of 2.0 mol L<sup>-1</sup> methanol and a H<sub>2</sub>-0.5% CO mixture. The voltammogram in the absence of contaminants shows relatively few features: anodic–cathodic peaks in the 0.4–0.7 V/NHE region, ascribed to the Vulcan® support; a hydrogen adsorption/desorption and evolution (~0.0–0.15 V/NHE) region, as well as the first stage of an O<sub>2</sub> evolution process (~0.9–1.0 V/NHE). No electrochemical signs of decomposition processes, such as decarbonylation, were observed (the stability of the electrode was evaluated upon continuous cycling over a several hour period).

On the other hand, the cyclic voltammograms of Rh<sub>6</sub>(CO)<sub>16</sub>/Vulcan® are very little affected by the presence of methanol or CO, with practically no oxidation peaks of both contaminants being observed. In contrast, Pt is well known to oxidise both compounds [2,3].

Fig. 2a shows typical ORR current–potential curves of Rh<sub>6</sub>(CO)<sub>16</sub>/Vulcan®, in the absence and presence of 1 and 2 mol L<sup>-1</sup> methanol. It can be observed that the cluster shows a charge-transfer kinetic control region above 0.76 V/NHE; the mixed kinetic-diffusion control region is observed in the 0.56–0.74 V/NHE range, while at more cathodic potentials a diffusion plateau is well defined. On the other hand, the current–potential curves of Rh<sub>6</sub>(CO)<sub>16</sub> practically do not change in the presence of methanol; in contrast, a notorious performance decrease has been reported for Pt/Vulcan® electrodes in the presence of methanol at these concentrations [15]. According to the Koutecky–Levich analysis for Rh<sub>6</sub>(CO)<sub>16</sub> (inset 1, Fig. 2a), it may be suggested that the ORR follows a *direct*, four electron pathway to water formation, without an important production of a hydrogen peroxide intermediary, even in the presence of methanol. The kinetic parameters were calculated from the corresponding mass-transfer corrected Tafel plots (inset 2, Fig. 2a) and listed in Table 1, along with the open circuit potentials and reaction order values (*m*). The open circuit potential, E<sub>oc<sup>2</sup></sub>, was around 0.83 V/NHE and did not practically change with methanol. The reaction order, *m*, calculated from the slope of the log *i* vs. log [1 – (*i*/*i*<sub>d</sub>)] plots for several rotation rates at a given potential [16] is virtually *one* with respect to oxygen in all cases. The Tafel slope (*b*) and charge-transfer coefficient (*α*), related with the reaction mechanism and free energy decrease, respectively [17], did not change significantly with the presence of methanol. All

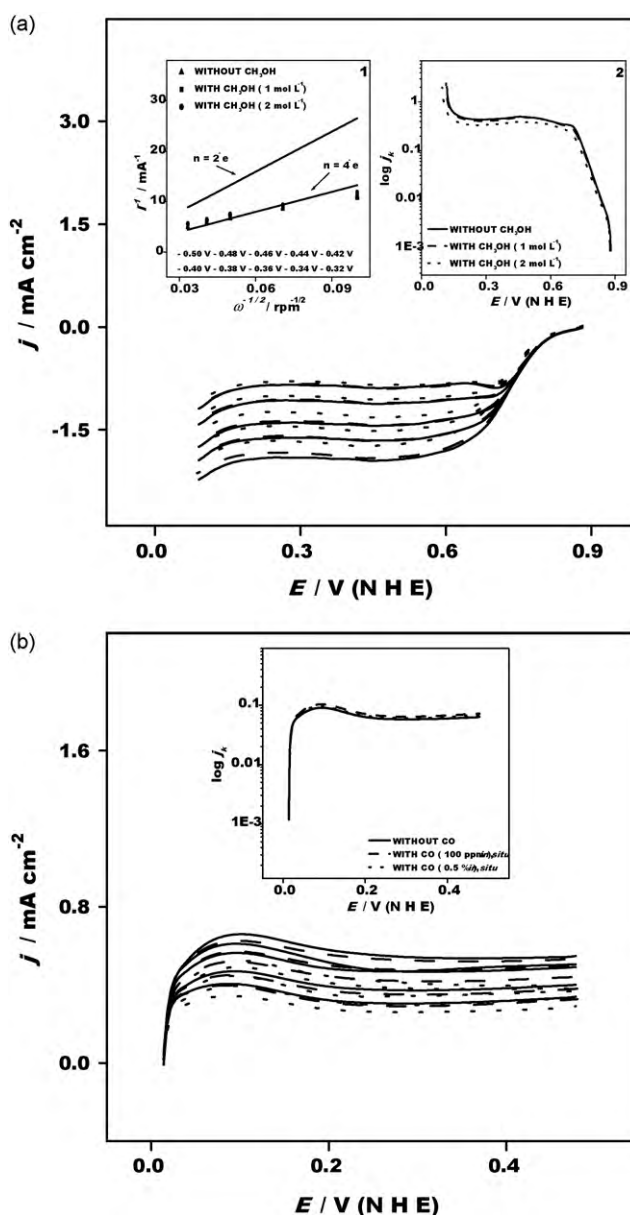


Fig. 2. (a) ORR current–potential curves of Rh<sub>6</sub>(CO)<sub>16</sub>/Vulcan® without methanol (-), with 1 mol L<sup>-1</sup> methanol (- -) and with 2 mol L<sup>-1</sup> methanol (.....); insets 1 and 2 show the corresponding Koutecky–Levich and mass-transfer corrected Tafel plots, respectively. (b) HOR current–potential curves of Rh<sub>6</sub>(CO)<sub>16</sub>/Vulcan® without CO (-), with 100 ppm CO (- -) and with 0.5% CO (.....); the inset shows the corresponding mass-transfer corrected Tafel plots.

the exchange current density (*j*<sub>0</sub>) values are one order of magnitude higher than that for Pt/Vulcan® under similar conditions [18]; this is a very important feature, considering the direct relation of this parameter with the ORR rate constant [17]. In summary, the compound Rh<sub>6</sub>(CO)<sub>16</sub> exhibits an important electrocatalytic activity for the ORR that has not been considered before, with important resistance properties to methanol. Rh metal particles, on the other hand, also show electrocatalytic activity for the ORR, however, they exhibit undesired effects of surface oxidation and their methanol tolerance has been reported as much less (0.1 mol L<sup>-1</sup>) [19] than that presented by the carbonyl studied in this work. Rh<sub>6</sub>(CO)<sub>16</sub> also shows a higher methanol resistance degree than most catalysts reported for this purpose [4,7,11,20–24].

Fig. 2b shows the HOR current–potential curves for Rh<sub>6</sub>(CO)<sub>16</sub>/Vulcan®, in the absence and presence of carbon

**Table 1**

Open circuit potential, reaction order and average kinetic parameters of  $\text{Rh}_6(\text{CO})_{16}/\text{Vulcan}^{\text{®}}$  for the oxygen reduction reaction (ORR) in the absence and presence of methanol and for the hydrogen oxidation reaction (HOR) in the absence and presence of carbon monoxide.

Reaction	Contaminant present (mol L <sup>-1</sup> )	Open circuit potential $E_{oc}^{O_2}$ (V/NHE)	$m$	$b$ (mV dec <sup>-1</sup> )	$a$	$j_0$ (mA cm <sup>-2</sup> )
ORR	[CH <sub>3</sub> OH] = 0.0	0.83	0.98	83.60	0.72	$2.25 \times 10^{-5}$
	[CH <sub>3</sub> OH] = 1.0	0.83	0.99	82.11	0.73	$2.75 \times 10^{-5}$
	[CH <sub>3</sub> OH] = 2.0	0.83	1.00	81.22	0.74	$2.84 \times 10^{-5}$
Reaction	Contaminant present	Open circuit potential $E_{oc}^{H_2}$ (V/NHE)	$m$	$b$ (mV dec <sup>-1</sup> )	$a$	$j_0$ (mA cm <sup>-2</sup> )
HOR	[CO] = 0.0	0.0	–	41.03	0.46	0.3127
	[CO] = 100 ppm ( <i>in situ</i> )	0.0	–	41.20	0.46	0.2542
	[CO] = 0.5% ( <i>in situ</i> )	0.0	–	42.32	0.42	0.2453

monoxide. The kinetic parameters, calculated from the corresponding mass-transfer corrected Tafel plots (inset, Fig. 2b), are summarized in Table 1. As in the case of the ORR, the curves and the kinetic parameters related with the reaction pathway ( $b$  and  $\alpha$ ), virtually do not change with the presence of the fuel cell contaminant. As for the values of  $j_0$ , although they are somewhat smaller than those of Pt/Vulcan<sup>®</sup> ( $0.47 \text{ mA cm}^{-2}$ ) [18] and slightly decrease in the presence of CO, it is well known that Pt catalysts become deactivated even by ppm levels of CO [2]; hence, the Rh complex stands as a potential candidate to be evaluated as anode in reforming hydrogen PEM fuel cells, on the basis of the important tolerance degree to CO exhibited in this study.

#### 4. Conclusions

In conclusion, it was demonstrated that the rhodium carbonyl cluster  $\text{Rh}_6(\text{CO})_{16}$  can perform the oxygen reduction and hydrogen oxidation reactions in an acid medium, even in the presence of methanol (in concentrations as high as  $2 \text{ mol L}^{-1}$ ) and CO (0.5%, v/v), respectively. These resistance properties to common fuel cell contaminants make the Rh complex an interesting prospect to be used as cathode in direct methanol fuel cells (DMFCs) and as cathode and anode in reforming hydrogen PEM fuel cells. This compound exhibiting a *dual* electrocatalytic behavior (for both the ORR and HOR) has a well defined molecular and crystal structure and is a novelty in a field dominated by metal nanoparticles and other materials with rather complex and not clearly defined structures. The electrocatalytic properties of this complex most likely arise from its electron-rich rhodium atom core, with the carbonyl ligands exerting the observed protective effect against the poisoning agents and possibly against oxidation as well.

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#### References

- [1] T.R. Ralph, M.P. Hogarth, *Platinum Met. Rev.* 46 (2002) 3–14.
- [2] T.R. Ralph, M.P. Hogarth, *Platinum Met. Rev.* 46 (2002) 117–135.
- [3] T.R. Ralph, M.P. Hogarth, *Platinum Met. Rev.* 46 (2002) 146–164.
- [4] A.K. Shukla, R.K. Raman, in: K.-D. Kreuer, D.R. Clarke, M. Rühle, J.C. Bravman (Eds.), *Annual Review of Materials Research*, vol. 33, Annual Reviews, Palo Alto, 2003, pp. 155–168.
- [5] R.H. Castellanos, E. Borja-Arco, A. Altamirano-Gutiérrez, R. Ortega-Borges, Y. Meas, O. Jiménez-Sandoval, *J. New Mater. Electrochem. Syst.* 8 (2005) 69–75.
- [6] M. Bron, P. Bogdanoff, S. Fiechter, M. Hilgendorff, J. Radnik, I. Dorbandt, H. Schulenburg, H. Tributsch, *J. Electroanal. Chem.* 517 (2001) 85–94.
- [7] T.J. Schmidt, U.A. Paulus, H.A. Gesteiger, N. Alonso-Vante, R.J. Behm, *J. Electrochem. Soc.* 147 (2000) 2620–2624.
- [8] M. Bron, P. Bogdanoff, S. Fiechter, H. Tributsch, *J. Electroanal. Chem.* 578 (2005) 339–344.
- [9] R.H. Castellanos, A.L. Ocampo, P.J. Sebastian, *J. New Mater. Electrochem. Syst.* 5 (2002) 83–90.
- [10] G.Q. Sun, J.T. Wang, R.F. Savinell, *J. Appl. Electrochem.* 28 (1998) 1087–1093.
- [11] D. Chu, R. Jiang, *Solid State Ionics* 148 (2002) 591–599.
- [12] E.R. Corey, L.F. Dahl, *J. Am. Chem. Soc.* 85 (1963) 1202–1203.
- [13] D.H. Farrar, E.V. Grachova, A. Lough, C. Patirana, A.J. Poë, S.P. Tunik, *J. Chem. Soc. Dalton Trans.* 13 (2001) 2015–2019.
- [14] P. Gelin, Y. Ben Taarit, C. Naccache, *J. Catal.* 59 (1979) 357–364.
- [15] E. Borja-Arco, R.H. Castellanos, J. Uribe-Godínez, A. Altamirano-Gutiérrez, O. Jiménez-Sandoval, *J. Power Sources* 188 (2009) 387–396.
- [16] T. Jiang, G.M. Brisard, *Electrochim. Acta* 52 (2007) 4487–4496.
- [17] E. Gileadi, *Electrode Kinetics*, VCH Publishers, New York, 1993.
- [18] J. Uribe-Godínez, R.H. Castellanos, E. Borja-Arco, A. Altamirano-Gutiérrez, O. Jiménez-Sandoval, *J. Power Sources* 177 (2008) 286–295.
- [19] D. Cao, A. Wieckowski, J. Inukai, N. Alonso-Vante, *J. Electrochem. Soc.* 153 (2006) A869–A874.
- [20] N. Alonso-Vante, P. Bogdanoff, H. Tributsch, *J. Catal.* 190 (2000) 240–246.
- [21] H. Tributsch, M. Bron, M. Hilgendorff, H. Schulenburg, I. Dorbandt, V. Eyert, P. Bogdanoff, S. Fiechter, *J. Appl. Electrochem.* 31 (2001) 739–748.
- [22] A.L. Ocampo, R.H. Castellanos, P.J. Sebastian, *J. New Mater. Electrochem. Syst.* 5 (2002) 163–168.
- [23] R.-F. Wang, S.-J. Liao, H.-Y. Liu, H. Meng, *J. Power Sources* 171 (2007) 471–476.
- [24] R. Jiang, D. Chu, *J. Electrochem. Soc.* 147 (2000) 4605–4609.