Journal of Power Sources 196 (2011) 1103–1106

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

Polyaniline/carbon black composite-supported iron phthalocyanine as an oxygen reduction catalyst for microbial fuel cells

Yong Yuan[a,*], Jalal Ahmed[b], Sunghyun Kim[b,**]

[a] Guangdong Institute of Eco-environmental and Soil Sciences, Guangzhou 510650, China
[b] Department of Bioscience and Biotechnology, Konkuk University, Seoul 143-701, Republic of Korea

ARTICLE INFO

Article history:
Received 21 July 2010
Received in revised form 28 August 2010
Accepted 31 August 2010
Available online 8 September 2010

Keywords:
Polyaniline/carbon black
Microbial fuel cell
Iron phthalocyanine
Platinum

ABSTRACT

Polyaniline/carbon black (PANI/C) composite-supported iron phthalocyanine (FePc) (PANI/C/FePc) has been investigated as a catalyst for the oxygen reduction reaction (ORR) in an air–cathode microbial fuel cell (MFC). The electrocatalytic activity of the PANI/C/FePc toward the ORR is evaluated using cyclic voltammogram and linear scan voltammogram methods. In comparison with that of carbon-supported FePc electrode, the peak potential of the ORR at the PANI/C/FePc electrode shifts toward positive potential, and the peak current is greatly increased, suggesting the enhanced activity of FePc absorbed onto PANI/C. Additionally, the results of the MFC experiments show that PANI/C/FePc is well suitable to be the cathode material for MFCs. The maximum power density of 630.5 mW m^{-2} with the PANI/C/FePc cathode is higher than that of 336.6 mW m^{-2} with the C/FePc cathode, and even higher that that of 575.6 mW m^{-2} with a Pt cathode. Meanwhile, the power per cost of the PANI/C/FePc cathode is 7.5 times greater than that of the Pt cathode. Thus, the PANI/C/FePc can be a potential alternative to Pt in MFCs.

1. Introduction

Microbial fuel cells (MFCs) are devices that convert organic substrates into electricity with the aid of microorganisms as catalysts. Since they can directly generate electricity from various wastes, increasing attentions have been paid to their development and improvement in recent years [1–3]. In MFCs, an electron acceptor is employed to receive the electrons transferred from the anode to complete the electric circuit. Oxygen is the most sustainable electron acceptor currently available for MFC cathodes. However, the oxygen reduction reaction (ORR) requires an efficient catalyst to overcome the high overpotential for reduction to water. At present, platinum (Pt) has been commonly used as the efficient catalyst of ORR in MFCs. It has been already noted that the high cost of an MFC mostly comes from the high price of Pt, which has been severely hindering the commercial MFC applications. Hence, the development of new materials with high catalytic properties to perform oxygen reduction is presently a challenge of great technological importance in MFCs. Iron phthalocyanine (FePc) had been firstly examined as an alternative to Pt [4]. Prior to being employed to the cathode of an MFC, FePc was firstly adsorbed onto carbon black support materials. Yu et al. discovered that the performance of a FePc cathode strongly depended on the carbon support materials in MFCs [5]. In addition to Vulcan XC carbon and Ketjenblack carbon, however, few support materials have been evaluated for a FePc cathode [6].

Conductive polymer, such as polyaniline (PANI) has attracted great interests since being electrochemically synthesized for the first time more than two decades ago. Due to its interesting properties, such as environmental stability, ease of synthesis and high conductivity at room temperature, PANI shows great potential for application in the preparation of actuators, chemical sensors, biosensors and electronic devices [7,8]. Previous studies demonstrated that PANI was an efficient matrix for the immobilization of the ORR catalysts, such as Pt, cobalt and MnO_2, due to the increased electrochemical surface area and the improved electrocatalytic ability of catalysts [9–11]. However, negligible attention has been paid to the application of PANI for supporting metal complex to act as an efficient catalyst of ORR. In this study, we proposed to use polyaniline/carbon black (PANI/C) as an electrocatalyst support for ORR of FePc in an air–cathode single-chamber MFC. The electrocatalytic activities of PANI/C-supported FePc were investigated with voltammograms. The performance of power generation and the cost effect with the proposed cathode were compared with various cathodic catalysts including PANI/C alone, carbon black-supported FePc (C/FePc), and Pt.

2. Experimental

2.1. Preparation of cathodes

An air cathode was constructed as previously proposed by Chen et al. with a water proof and a catalytic layer coating on the both

---

* Corresponding author. Tel.: +86 20 87025101; fax: +86 20 87025101.
** Corresponding author. Tel.: +82 2 4503378; fax: +82 2 4503378.
E-mail addresses: yuanyong@soil.gd.cn (Y. Yuan), skim100@konkuk.ac.kr (S. Kim).

0378-7753/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2010.08.112

side of a wet-proofed carbon cloth [12]. The catalytic layer was produced as follows: 7 mg PANI/C (Sigma–Aldrich, 20 wt% PANI content, doped with proprietary organic sulfonic acid) was dispersed in 1 mL methanol containing 7 mg FePc. The mixture was ultrasonicated for 5 min followed by 1 h of vigorous agitation, and then 0.25 mL Nafion solution was added before the resulted ink was coated on 30% wet-proofed carbon cloth (type B, E-Tek) on whose side gas diffusion layer coating was not made, resulting in 1 mg cm^{-2} PANI/C/FePc loading. The same procedure was followed to make C/FePc, and Pt cathodes. All electrodes were dried at 70 °C in an oven for at least 2 h before use.

2.2. MFC configuration and operation

Air–cathode single-chamber MFCs with an inner volume of 12 mL were constructed as reported previously [13]. A cylindrical MFC chamber with a length of 1.7 cm and a diameter of 3.0 cm was made of plexiglass. Both anode and cathode surface area were 7 cm^2. Non-wet proofing carbon cloth (type A, E-Tek) was used as an anode without further treatment. The anode and cathode were placed on opposite sides with the oxygen catalyst coating layer facing to the anode and the polytetrafluoroethylene (PTFE) coated gas diffusion layer facing to air.

Reactors were inoculated with 2 mL activated sludge (Liede wastewater treatment plant, Guangzhou, China) and 10 mL glucose (1000 mg L^{-1}) culture medium solution. The culture medium solution contained: KH_2PO_4 (13.6 g L^{-1}), NaOH (2.32 g L^{-1}), NH_4Cl (0.31 g L^{-1}), NaCl (1.0 g L^{-1}), a vitamin stock solution (12.5 mL L^{-1}) and a mineral stock solution (12.5 mL L^{-1}) [14]. Power density curves were obtained by changing the circuit resistor from 98 to 7600 Ω, with a single resistor used for a full batch cycle. The medium in the reactor was refilled when the voltage dropped below 50 mV. All tests were conducted in batch mode in a 30 °C incubator. The power was normalized by the projected surface area of the cathode. All tests were conducted in duplicate, and mean values are presented.

2.3. Electrochemical measurements

In order to investigate the ORR characterization of various catalysts, cyclic voltammogram (CV) and linear sweep voltammogram (LSV) were performed with the conventional three-electrode system. A Pt wire and a saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. The catalysts coated glassy carbon (GC, 3.0 mm diameter) electrodes were used as working electrodes. All electrochemical measurements were conducted with 50 mM phosphate buffer as an electrolyte.

3. Results and discussion

3.1. Catalytic activity of PANI/C/FePc toward ORR

Previous studies showed that the electricity generation capability of pyrolysed FePc cathode was similar to that of a Pt cathode in an MFC [6]. However, the ORR mechanisms and active sites in the pyrolysed FePc still remain under debate [15–18]. Meanwhile, considering the complex procedures and the intensive energy demand for pyrolysing, FePc was used as received without any pyrolysis in this study. Although the conductivity of PANI was rather high, the conductive of the polymer would be further improved when it was composited with high conductive materials such as carbon black according to previous report by Wu et al. [19], which would benefit the fuel cell performances. Therefore, the composite instead of the polymer alone was applied in the present study.

Fig. 1A shows that two couple of typical redox peaks appeared on the CV of PANI/C/FePc with redox potentials of +0.16 V (vs. SCE)

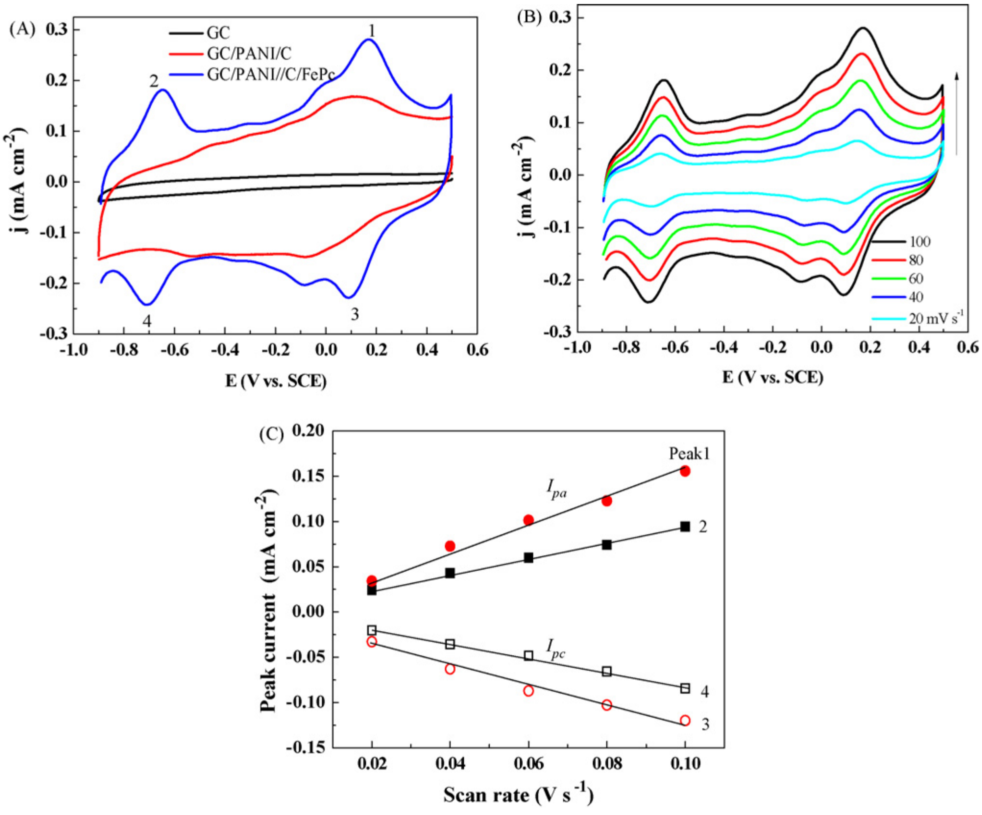

Fig. 1. Cyclic voltammetric characterizations of PANI/C and PANI/C/FePc at a scan rate of 100 mV s^{-1} (A), CVs of PANI/C/FePc with different scan rates (B) and the peak currents as a linear function of scan rates(C). The peak 1–4 was in accordance with the marks in graph A.

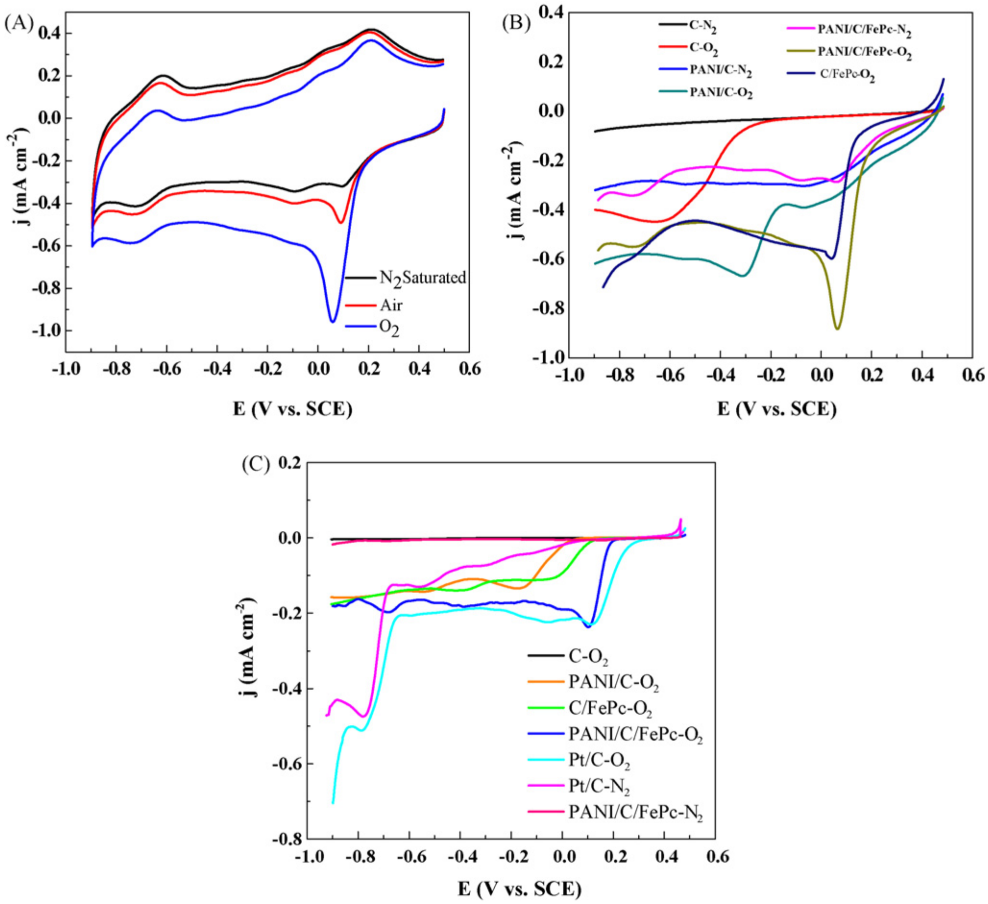

Fig. 2. CV (A) and LSV of various electrodes for the oxygen reduction at scan rate of 100 mV s^{-1} (B) and 1 mV s^{-1} (C)

and −0.67 V (vs. SCE), respectively. Since these two redox peaks were not discovered from the PANI/C electrode, they were highly believed to belong to FePc. According to previous study, the redox peak at +0.16 V was caused by the redox reaction of phthalocyanine ligand $[Fe(III)Pc(-2)]^+/Fe(II)Pc(-2)$,and the redox peak at −0.67 V was due to the redox reaction of $Fe(II)Pc(-2)/[Fe(II)Pc(-3)]^-$ [20]. Fig. 1B shows the cyclic voltammograms of PANI/C/FePc with different scan rates (from 20 to 100 mV s^{-1}). A linearity of the cathodic or anodic peak currents with scan rates indicated that the redox reaction of FePc was a diffusionless surface-controlled process, confirming that the immobilized PANI/C/FePc was rather stable (Fig. 1C).

The activity of various cathodes toward ORR was conducted with both CV and LSV in 50 mM PBS solution. As shown in Fig. 2A, a new reduction peak was discovered when the CV was conducted in O_2-saturated solution. It could be readily determined that the oxygen reduction was mainly associated with the reduction of $[Fe(III)Pc(-2)]^+$ at +0.095 V due to the appearance of oxygen reduction peak at the same potential. A peak potential of +0.062 V (vs. SCE) and a peak current of 0.60 mA cm^{-2} were observed on the LSV of PANI/C/FePc, which was more positive and greater than those of PANI/C (−0.31 V and 0.38 mA cm^{-2}), C/FePc (0.04 V and 0.36 mA cm^{-2}) and carbon black (−0.64 V and 0.32 mA cm^{-2}) electrodes (Fig. 2B), indicating that the PANI/C/FePc had the most catalytic activity toward ORR. It was also worth noting that the oxygen reduction potential of PANI/C/FePc was slightly positive over that of C/FePc, and the peak current was almost two times higher than that of C/FePc, supporting that PANI/C was a better support material than carbon black alone in terms of the catalytic activity of ORR. The LSV of ORR on various electrodes at a low scan rate of 1 mV s^{-1} was also investigated as shown in Fig. 2C. The electrochemical activity of PANI/C/FePc toward ORR was comparable with Pt/C in low voltages. It is well known that ORR process involves H^+ consumption. H^+-donated PANI under a neutral condition could improve the kinetics of the catalytic reaction by supplying an H^+ accumulated environment around FePc [21]. In addition, FePc as an insulating material only in contact with the electrode was active for the electrocatalysis [22]. When FePc was confined in PANI matrix, the electrochemical catalysis was expected to occur throughout the polymer layer, which was thought to be more active according to previous studies [23]. Meanwhile, an obvious catalyzed oxygen reduction peak appeared on the LSV of a PANI/C cathode, suggesting that PANI alone possessed the catalytic activity toward ORR. Khomenko et al. demonstrated that the carbon atoms on aniline ring could supply active sites for oxygen chemical adsorption, which could weaken the O–O bond of oxygen and lower the activation energy for reduction [24]. Thus, the coordination of PANI to FePc would be also possible to cause an increase of the catalytic activity toward ORR.

3.2. *The performance of MFCs with different cathodic catalysts*

With the proposed cathode, bioelectricity was successfully obtained from an air–cathode single-chamber MFC inoculated with sewage sludge. The power density versus current density curves were presented in Fig. 3. The maximum power density of 650.5 mW m^{-2} achieved from an MFC with the PANI/C/FePc cathode was higher than those from MFCs with carbon black (93.9 mW m^{-2}), PANI/C (401.8 mW m^{-2}), C/FePc (336.6 mW m^{-2}), and even Pt (575.6 mW m^{-2}) cathodes (Fig. 3A). This result strongly

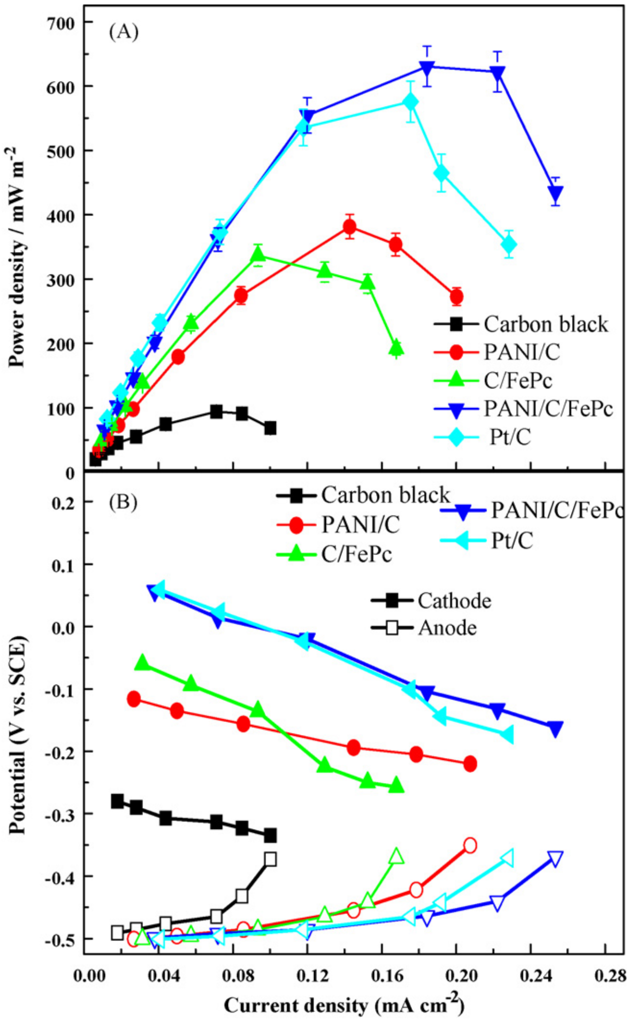

Fig. 3. Power density curves (A) and individual potentials of anode (open symbol) and cathode (filled symbol) (B).

suggests that PANI/C/FePc will be a good alternative to Pt in MFCs. Fig. 3B shows the curves of the individual cathode or anode potential versus current density. The anode potentials of various MFCs are almost consistent while the cathode potentials vary. An obvious increased cathode potential under almost all currents was obtained compared with those with the carbon black, PANI/C, C/FePc, and even Pt cathodes, indicating that the difference on the MFC performances mainly resulted from the variation of the catalytic activity of the catalysts in cathodes.

3.3. *Cost of cathode materials*

As mentioned above, practical applications of MFCs are limited by high cost. Thus, it is critical to replace the noble Pt by other cheap and efficient oxygen reduction catalysts. The comparison of the cathode costs is listed in Table 1. The PANI/C/FePc cathode produced rather high power per dollar (4.11 mW \$$^{-1}$), which was 7.5 times greater than that of Pt/C (0.55 mW \$$^{-1}$). Due to this huge economic advantage, the PANI/C/FePc could be a good alternative to Pt in MFCs. Although the highest power per dollar was achieved from a PANI/C cathode, the low energy output might limit its' practical application.

Table 1
Comparison of the cost of cathode materials.

Cathode material	Price (\$ g^{-1})[a]	Power density (mW m^{-2})	Power per cost of cathode material (mW \$$^{-1}$)
C/FePc	7.42	336.6	3.17
PANI/C	3.39	381.8	7.78
PANI/C/FePc	10.74	630.5	4.11
Pt/C	29.38	575.6	0.55

[a] Normalized to cathode materials.

4. Conclusions

In this study, PANI/C was proved to be efficient for supporting the ORR catalyst FePc in an air–cathode MFC. With the proposed cathode, the maximum power density of 630.5 mW m^{-2} was the highest one among those cathodes including PANI/C, C/FePc, and Pt. Meanwhile, the power per cost of PANI/C/FePc was 7.5 times higher than that of Pt. The results demonstrated that the PANI/C was an ideal supporting material for FePc and the PANI/C/FePc offered a good alternative to Pt in MFC practical applications.

Acknowledgment

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) (No. 2010-0009725).

References

[1] H. Liu, R. Ramnarayanan, B.E. Logan, Environ. Sci. Technol. 38 (2004) 2281–2285.
[2] B.E. Logan, Water Sci. Technol. 52 (2005) 31–37.
[3] B.K. Min, J.R. Kim, S.E. Oh, J.M. Regan, B.E. Logan, Water Res. 39 (2005) 4961–4968.
[4] F. Zhao, F. Harnisch, U. Schröder, F. Scholz, P. Bogdanoff, Electrochem. Commun. 7 (2005) 1405–1410.
[5] E.H. Yu, S. Cheng, K. Scott, B.E. Logan, J. Power Sources 171 (2007) 275–281.
[6] S.N.S. Goubert-Renaudin, X.l. Zhu, A. Wieckowski, Electrochem. Commun. (2010), doi:10.1016/j.elecom.2010.06.004.
[7] R.V. Parthasarathy, C.R. Martin, Nature 369 (1994) 298–301.
[8] H. Adam, M. Agata, A. Lewenstam, Talanta 41 (1994) 323–325.
[9] C. Coutanceau, M.J. Croissant, T. Napporn, C. Lamy, Electrochim. Acta 46 (2000) 579–588.
[10] H. Nguyen Cong, K. El Abbassi, P. Chartier, Electrochem. Solid-State Lett. 3 (2000) 192–195.
[11] R. Bashyam, P. Zelenay, Nature 443 (2006) 63–66.
[12] S. Cheng, H. Liu, B.E. Logan, Electrochem. Commun. 8 (2006) 489–494.
[13] H. Liu, B.E. Logan, Environ. Sci. Technol. 38 (2004) 4040–4046.
[14] D.R. Lovley, E.J.P. Phillips, Appl. Environ. Microbiol. 54 (1988) 1472–1480.
[15] T.S. Olson, S. Pylypenko, J.E. Fulghum, P. Atanassov, J. Electrochem. Soc. 157 (2010) B54–B63.
[16] S. Pylypenko, S. Mukherjee, T.S. Olson, P. Atanassov, Electrochim. Acta 53 (2008) 7875–7883.
[17] M. Lefevre, J.P. Dodelet, P. Bertrand, J. Phys. Chem. B 106 (2002) 8705–8713.
[18] M. Lefevre, J.P. Dodelet, P. Bertrand, J. Phys. Chem. B 104 (2000) 11238–11247.
[19] G. Wu, L. Li, J.H. Li, B.Q. Li, Carbon 43 (2005) 2579–2587.
[20] S. Ha, S. Kim, J. Electroanal. Chem. 468 (1999) 131–138.
[21] T. Abea, M. Kanekob, Prog. Polym. Sci. 28 (2003) 1441–1488.
[22] A. Eizing, A. Van Der Putten, W. Visscher, E. Barendrecht, J. Electroanal. Chem. 200 (1986) 313–322.
[23] C. Coutanceau, P. Crouifneau, J.M. Léger, C. Lamy, J. Electroanal. Chem. 379 (1994) 389–397.
[24] V.G. Khomenko, V.Z. Barsukov, A.S. Katashinskii, Electrochim. Acta 50 (2005) 1675–1683.