Short communication

An *in situ* Fourier transform infrared spectroelectrochemical study on ethanol electrooxidation on Pd in alkaline solution

Xiang Fang[a], Lianqin Wang[a], Pei Kang Shen[a,*], Guofeng Cui[b], Claudio Bianchini[c,*]

[a] The State Key Laboratory of Optoelectronic Materials and Technologies, School of Physics and Engineering, Sun Yat-Sen University, Guangzhou 510275, China
[b] School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China
[c] Istituto di Chimica dei Composti Organometallici (ICCOM-CNR), via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy

ARTICLE INFO

ABSTRACT

The mechanism of ethanol electrooxidation on a palladium electrode in alkaline solution (from 0.01 to 5 M NaOH) has been investigated by cyclic voltammetry and *in situ* Fourier transform infrared spectro-electrochemistry. The electrode performance has been found to depend on the pH of the fuel solution. The best performance was observed in 1 M NaOH solution (pH = 14), while the electrochemical activity decreased by either increasing or decreasing the NaOH concentration. *In situ* FTIR spectroscopic measurements showed the main oxidation product to be sodium acetate at NaOH concentrations higher than 0.5 M. The C–C bond cleavage of ethanol, put in evidence by the formation of CO_2, occurred at pH values ≤13. In these conditions, however, the catalytic activity for ethanol oxidation was quite low. No CO formation was detected along the oxidation of ethanol by FTIR spectroscopy.

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1. Introduction

Increasing research efforts are currently being made to develop efficient direct ethanol fuel cells (DEFCs), due to many advantages of ethanol over other fuels, among which there are its high energy density, easy storage, low toxicity and renewable character [1]. The vast majority of anode electrocatalysts for DEFCs are still based on Pt, alone or alloyed with other metals such as Ru and Sn [2–8]. All Pt-based catalysts are deactivated by the formation of strong bonds to CO and CO-like species, which ultimately results in the use of high metal loadings to ensure an acceptable cell durability. In addition to this shortcoming, Pt-based electrocatalysts promote the oxidation of ethanol only in acidic media with consequent chemical stress of many components of the cell hardware. Recently, Pd-based catalysts have aroused much attention because they can be highly active for the ethanol oxidation in alkaline media where many non-noble metals are stable for electrochemical applications [9–16]. The dilution of Pd with non-noble metals is expected to decrease remarkably the anode cost and hence allow for an effective commercialization of DEFCs, especially for portable electronic devices. Despite the progress achieved in the design and develop-

ment of Pd-based anode electrocatalysts and of the relative DEFCs [15,16], very few mechanistic studies on the electrooxidation of ethanol on Pd have been reported so far and mostly based on *extra situ* experiments [14–16], theoretical analysis [17] or cyclic voltammetry [18,19]. Herein, we describe the results of an *in situ* FTIR spectroelectrochemical study [20,21] of the ethanol oxidation on Pd in alkaline solution in which particular attention has been devoted to the effect of the pH.

2. Experimental

All solutions were prepared using deionized water (18.3 MΩ cm^{-1}) and analytical grade chemicals. The ethanol concentration was fixed at 1 M. Electrolytes with different NaOH concentrations were used to investigate the pH effect on the ethanol electrooxidation. When necessary, $NaClO_4$ was added to the NaOH solutions to maintain a constant ionic strength. All solutions were purged with nitrogen prior to use.

An electrochemical cell equipped with a CaF_2 window was used for the electrochemical and *in situ* FTIR electrospectroscopic measurements. The working electrode was a palladium electrode with a 6 mm diameter. A platinum foil and an Hg/HgO electrode were used as the counter and reference electrode, respectively. The electrochemical measurements were performed on a 263A potentiostat/galvanostat (EG&G-PARC, USA), connected to the FTIR spectrometer (Nicolet 5700 with DTGS detector, Thermo Electron Corporation, USA). The measurements were carried out at 25 °C.

* Corresponding authors. Tel.: +86 20 84036736; fax: +86 20 84113369.
E-mail addresses: stsspk@mail.sysu.edu.cn (P.K. Shen),
claudio.bianchini@iccom.cnr.it (C. Bianchini).

Prior to each experiment, the palladium electrode was polished with alumina powder, followed by a supersonic rinsing in pure water and a potential cycling in 0.1 M HClO$_4$ at 0.1 V s^{-1} between 0.242 and 1.2 V vs. SCE. After the palladium electrode was immersed into the electrochemical cell. During the *in situ* FTIR spectroelectrochemical experiments, the electrode was pressed against the CaF$_2$ window to form a thin layer solution. Each infrared spectrum was recorded from 128 interferograms at the resolution of 4 cm^{-1}. The reference spectrum (R_{ref}) was collected at 0.024 V vs. SCE. The electrode potentials were increased by 0.1 V intervals from the reference potential up to 1.124 V and then decreased back to the initial potential. The equilibrium at each potential was achieved in 5 s before the collection of the sample spectra (R_s). Each final spectrum was reported using Eq. (1). Accordingly, the negative bands represent the species produced and the positive bands the species consumed.

$$\frac{\Delta R}{R} = \frac{R_s - R_{ref}}{R_{ref}} \qquad (1)$$

All the potentials in the figures were quoted with respect to the reversible hydrogen electrode (RHE).

3. Results and discussion

The effect of the pH on the ethanol electrooxidation was investigated by cyclic voltammetry (CV) using 1 M ethanol solutions with different NaOH concentrations but ionic strengths similar to that of 1 M NaOH (Fig. 1).

From a perusal of this figure one may readily realize that the Pd electrode exhibits the highest catalytic activity in 1 M NaOH solution, while the oxidation activity decreases for NaOH concentrations lower or higher than 1 M. Already at pH 12, the activity was extremely low. These results are consistent with the inactivity of Pd-based electrocatalysts for ethanol oxidation in acidic solution [22] and with the observation that a too high coverage of the Pd surface with hydroxyl groups disfavors the adsorption of ethanol [18].

In situ FTIR electrospectroscopy was used to gain insight into the mechanism of the ethanol electrooxidation on Pd at different pH values (Fig. 2). At NaOH concentrations ≥0.5 M, only the characteristic bands of the acetate ion (1558 and 1415 cm^{-1}) were observed (Fig. 2a–d), which confirms the selectivity of ethanol oxidation on Pd in strong alkaline media [14–16]. This finding contrasts with the behavior of Pt-based electrocatalysts in acidic media that invariably oxidize ethanol to mixtures of acetic acid, acetaldehyde and CO$_2$ [23,24].

At pH values lower than 13.3, the FTIR spectra showed the appearance of a band at 2343 cm^{-1}, which can be safely attributed to CO$_2$ formation, whose intensity increased by decreasing the pH (Fig. 2e and f). A carbonate ion band (1370 cm^{-1}) was not clearly visible in the spectra of Fig. 2e and f due to overlapping with the acetate band at 1415 cm^{-1}, yet its presence was inferred from the extensive broadening of the latter band. Parallel to the increase of the CO$_2$ band with decreasing pH, the acetate bands decreased in intensity: there was no acetate band during the forward potential step at 0.05 M NaOH (Fig. 2f). In Fig. 2f, the band at ca. 1400 cm^{-1} is larger and broader than that at 1558 cm^{-1}, which might be due to overlapping of the acetate band at 1415 cm^{-1} with the carbonate anion band at 1370 cm^{-1}. It is worth commenting that the oxidation of ethanol to CO$_2$ consumes 12 mol of OH$^-$ for each mol of ethanol. Accordingly, the pH may drop during the electrolysis in the thin layer; however, the oxidation of ethanol to acetate consumes 5 mol of OH$^-$ for each mol of ethanol so that the pH drop would be almost negligible for initial NaOH concentrations ≥1 M. At initial pH values lower than 13 (0.01 M NaOH), it is possible that the consumption of OH$^-$ groups leads to a decrease of the pH, but this effect, if occurring, contributes to demonstrate that the formation of CO$_2$ increases by decreasing the pH.

The IR region between 1700 and 3000 cm^{-1} is apparently affected by the concentration of OH$^-$ (water) in the thin layer between the electrode and the cell window. Accordingly, the band at 1650 cm^{-1} observed in the spectra acquired in 0.1, 0.05 and 0.01 M NaOH solutions, which appears as a shoulder in the spectra acquired at higher NaOH concentration, can be attributed to the diffusion of H$_2$O into the thin layer solution.

It is worth noticing that no trace of CO was detected even at the lowest NaOH concentration investigated. The experimental evidence accumulated indicates that the C–C bond cleavage of ethanol on Pd occurs only at NaOH concentrations lower than 0.5 M. Tentatively, we suggest that the ethanol oxidation to CO$_2$ on Pd in moderate alkaline media either proceeds with no intermediacy of CO$_{ads}$ (non-poisoning path) or by fast oxidation of weakly adsorbed CO by the abundant OH$^-_{ads}$ species. The latter eventuality is less likely in view of a specific study of CO electrooxidation on either Pt or Pt-based electrocatalysts recently reported by some of us where it was shown that the CO coverage on Pt is larger than that on Pd but the overpotential for CO oxidation is higher on Pd than on Pt [19]. On the other hand, other authors have reported that the IR detection of CO$_{ads}$ in an alkaline electrolyte is particularly difficult even for methanol oxidation on Pt [25,26]. In the present case, it is also possible that the detection of CO is made particularly difficult by its low concentration as the acetate is the largely major product.

Fig. 3a shows the potential dependence of the integrated intensities of the 1415 cm^{-1} band of the acetate produced in the thin layer solution. In the range of NaOH concentrations ranging from 0.5 to 5 M, the intensity of this band intensity increases above 0.4 V, reaching a maximum at about 0.8 V in the positive potential polarization. In the reverse process, the same band increases in intensity from 0.7 to 0.5 V. The observed variations of the integrated intensity of the band at 1415 cm^{-1} are consistent with the cyclic voltammograms shown in Fig. 1. It is also worth noticing that the ethanol oxidation in 1 M NaOH solution produces the largest amount of acetate. As the NaOH concentration was lowered to 0.1 M, the integrated band intensity showed a very low increase in the whole potential range investigated. Using a 0.05 M NaOH solution, we observed a growth of the integrated band intensity starting from the more positive potential of 1.1 V, while no trace of the acetate band was detected when the ethanol oxidation was carried out in a 0.01 M NaOH solution.
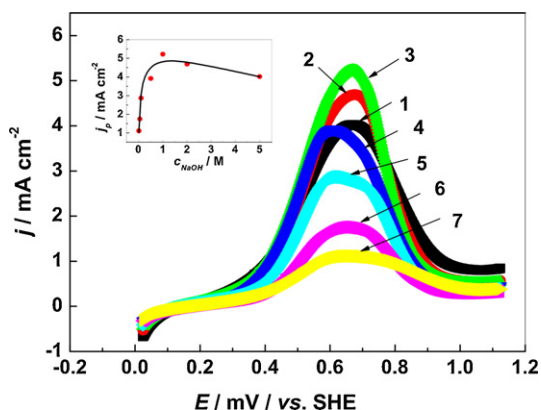

Fig. 1. Cyclic voltammograms of ethanol electrooxidation on Pd in 1 M ethanol containing different NaOH concentrations of (1) 5 M, (2) 2 M, (3) 1 M (pH = 14), (4) 0.5 M NaOH + 0.5 M NaClO$_4$ (pH = 13.3), (5) 0.1 M NaOH + 0.9 M NaClO$_4$ (pH = 13), (6) 0.05 M NaOH + 0.95 M NaClO$_4$ (pH = 12.7) and (7) 0.01 M NaOH + 0.99 M NaClO$_4$ (pH = 12). Sweep rate: 50 mV s^{-1}. The inset is the plot of peak current density against the NaOH concentration.
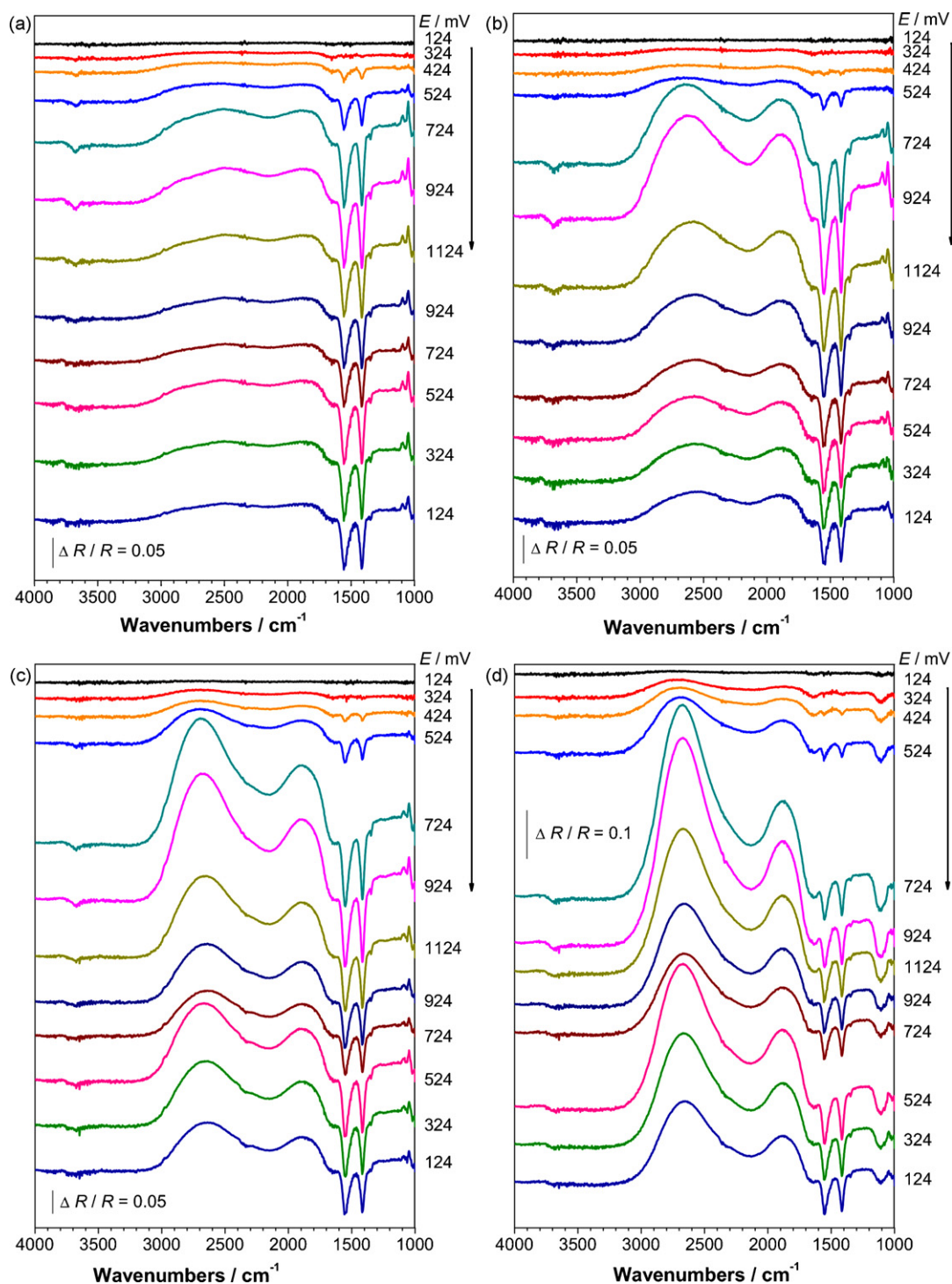
Fig. 2. *In situ* FTIR spectra obtained under potential step polarization in 1 M ethanol with different NaOH concentrations of (a) 5 M, (b) 2 M, (c) 1 M (pH = 14), (d) 0.5 M NaOH + 0.5 M NaClO$_4$ (pH = 13.3), (e) 0.1 M NaOH + 0.9 M NaClO$_4$ (pH = 13) and (f) 0.05 M NaOH + 0.95 M NaClO$_4$ (pH = 12.7). E_r = 24 mV, scan numbers: 128. The arrows indicate the potential polarization direction.

The integrated intensity of the band at 2343 cm^{-1} was used to estimate the amount of CO$_2$ produced during the ethanol oxidation at the pH values investigated. As shown in Fig. 3b, the amount of CO$_2$ increases steadily in the potential range from 0.5 to 0.9 V (forward polarization) and from 0.8 to 0.6 V (backward polarization) in alkaline solutions with NaOH concentrations lower than 0.1 M. The total amount of CO$_2$ produced in 0.1 and 0.05 M solutions were almost identical. In the 0.01 M NaOH solution, however, the formation of CO$_2$ was appreciable at a much more negative potential and the amount of CO$_2$ was larger than that observed for the experi-

ment performed in 0.1 or 0.05 M NaOH solutions. Apparently, the cleavage of the C–C bond is favored in dilute NaOH solutions where, on the other hand, low current densities are observed.

The mechanism of ethanol oxidation on a Pd disk electrode has been recently investigated by Zhao et al. by cyclic voltammetry [18]. The CV studies suggest that the rate determining step is the removal of the adsorbed acyl by the adsorbed hydroxyl, while the dissociative adsorption of ethanol proceeds quickly (Eqs. (2)–(4)).
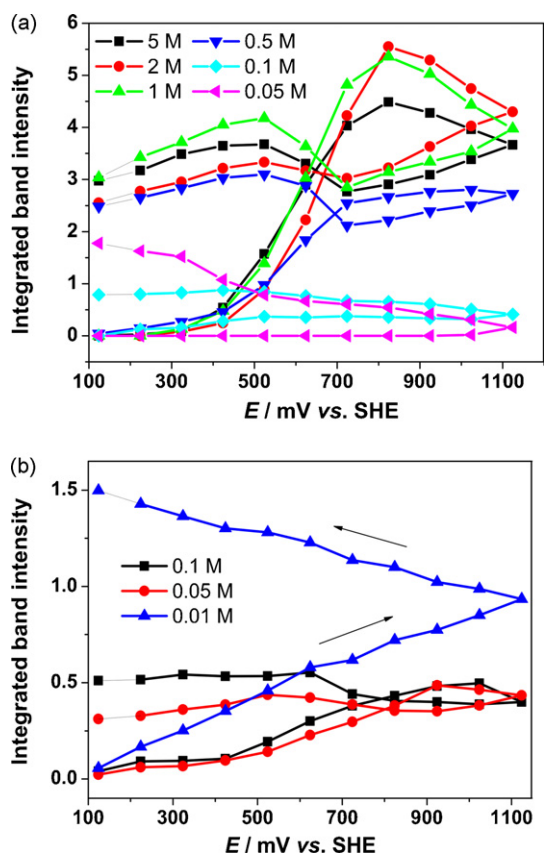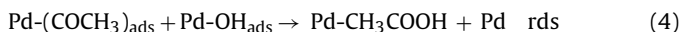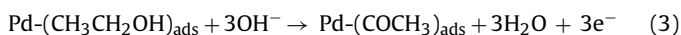
$$Pd + OH^- \rightarrow Pd\text{-}OH_{ads} + e^- \tag{2}$$

Fig. 3. (a) Dependence of the integrated band intensity at 1415 cm^{-1} on the polarization potential and (b) Plots of the integrated band intensity at 2343 cm^{-1} against the polarization potential.

$$Pd\text{-}(CH_3CH_2OH)_{ads} + 3OH^- \rightarrow Pd\text{-}(COCH_3)_{ads} + 3H_2O + 3e^- \quad (3)$$

$$Pd\text{-}(COCH_3)_{ads} + Pd\text{-}OH_{ads} \rightarrow Pd\text{-}CH_3COOH + Pd \quad rds \quad (4)$$

This study also confirms our assessment that a subtle balance of the EtOH and OH$^-$ concentrations is required for high oxidation activity as the neat prevalence of either species on the catalyst surface may hinder the adsorption of both species. In the same paper, it is also suggested that acetaldehyde is an active intermediate along the oxidation of ethanol on Pd, but its oxidation peak was not seen in any CV scan, which is in line with our results.

4. Conclusions

The ethanol electrooxidation on a Pd electrode was investigated by CV in alkaline media at different pH values and the products were analyzed by *in situ* FTIR spectroelectrochemistry. The Pd electrode showed a peak performance for the ethanol oxidation in 1 M NaOH (pH = 14), while at NaOH concentrations below or above 1 M the current density was invariably lower. The oxidation product was sodium acetate for NaOH concentrations higher than 0.5 M and the formation of CO$_2$ was observed exclusively for pH values equal to or lower than 13, which indicates that the Faradic efficiency of ethanol oxidation on Pd decreases by increasing the pH.

References

[1] H. Pramanik, Basu, Can. J. Chem. Eng. 85 (2007) 781.
[2] S. Song, P. Tsiakaras, Appl. Catal. B 63 (2006) 187.
[3] C. Lamy, A. Lima, V. LeRhun, F. Delime, C. Coutanceau, J.-M. Léger, J. Power Sources 105 (2002) 283.
[4] F. Vigier, S. Rousseau, C. Coutanceau, J.-M. Léger, C. Lamy, Top. Catal. 40 (2006) 111.
[5] G.A. Camara, R.B. de Lima, T. Iwasita, J. Electroanal. Chem. 585 (2005) 128.
[6] M. Watanabe, S. Motoo, J. Electroanal. Chem. 60 (1975) 267.
[7] J. Mann, N. Yao, A.B. Bocarsly, Langmuir 22 (2006) 10432.
[8] E. Antolini, Appl. Catal. B 74 (2007) 337.
[9] P.K. Shen, C.W. Xu, Electrochem. Commun. 8 (2006) 184.
[10] C.W. Xu, P.K. Shen, Y. Liu, J. Power Sources 164 (2007) 527.
[11] F.P. Hu, G.F. Cui, Z.D. Wei, P.K. Shen, Electrochem. Commun. 10 (2008) 1303.
[12] H.T. Zheng, Y.L. Li, S.X. Chen, P.K. Shen, J. Power Sources 163 (2006) 371.
[13] J. Liu, J. Ye, C.W. Xu, S.P. Jiang, Y.X. Tong, Electrochem. Commun. 9 (2007) 2334.
[14] V. Bambagioni, C. Bianchini, A. Marchionni, J. Filippi, F. Vizza, J. Teddy, P. Serp, M. Zhiani, J. Power Sources 190 (2009) 241.
[15] C. Bianchini, V. Bambagioni, J. Filippi, A. Marchionni, F. Vizza, P. Bert, A. Tampucci, Electrochem. Commun. 111 (2009) 1077.
[16] V. Bambagioni, C. Bianchini, J. Filippi, W. Oberhauser, A. Marchionni, F. Vizza, R. Psaro, L. Sordelli, M.L. Foresti, M. Innocenti, ChemSusChem 2 (2009) 99.
[17] G.F. Cui, S.Q. Song, P.K. Shen, A. Kowal, C. Bianchini, J. Phys. Chem. C 113 (2009) 15639.
[18] Z.X. Liang, T.S. Zhao, J.B. Xu, L.D. Zhu, Electrochim. Acta 54 (2009) 2203.
[19] F.P. Hu, C.L. Chen, Z.Y. Wang, G. Wei, P.K. Shen, Electrochim. Acta 52 (2006) 1087.
[20] A. Bewick, K. Kunimatsu, B.S. Pons, Electrochim. Acta 25 (1980) 465.
[21] K. Ashley, S. Pons, Chem. Rev. 88 (1988) 673.
[22] C.W. Xu, L. Cheng, P.K. Shen, Y.L. Liu, Electrochem. Commun. 9 (2007) 997.
[23] S. Rousseau, C. Coutanceau, C. Lamy, J.-M. Léger, J. Power Sources 158 (2006) 18.
[24] Q. Wang, G.Q. Sun, L.H. Jiang, Q. Xin, S.G. Sun, Y.X. Jiang, S.P. Chen, Z. Jusys, R.J. Behm, Phys. Chem. Chem. Phys. 9 (2007) 2686.
[25] E. Morallón, A. Rodes, J.L. Vázquez, J.M. Pérez, J. Electroanal. Chem. 391 (1995) 149.
[26] J.S. Spendelow, J.D. Goodpaster, P.J. Kenis, A.A. Wieckowski, Langmuir 22 (2006) 10457.