Short communication

Oxygen permeation through Nafion 117 membrane and its impact on efficiency of polymer membrane ethanol fuel cell

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ARTICLE INFO

ABSTRACT

We investigate oxygen permeation through Nafion 117 membrane in a direct ethanol fuel cell and elucidate how it affects the fuel cell efficiency. An obvious symptom of oxygen permeation is the presence of significant amounts of acetaldehyde and acetic acid in the mixture leaving anode when no current was drawn from the fuel cell (i.e. under the open circuit conditions). This parasitic process severely lowers efficiency of the fuel cell because ethanol is found to be directly oxidized on the surface of catalyst by oxygen coming through membrane from cathode in the absence of electric current flowing in the external circuit. Three commonly used carbon-supported anode catalysts are investigated, Pt, Pt/Ru and Pt/Sn. Products of ethanol oxidation are determined qualitatively and quantitatively at open circuit as a function of temperature and pressure, and we aim at determining whether the oxygen permeation or the catalyst's activity limits the parasitic ethanol oxidation. Our results strongly imply the need to develop more selective membranes that would be less oxygen permeable.

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1. Introduction

Direct ethanol fuel cells (DEFC), a subclass of polymer electrolyte membranes fuel cells (PEMFC) are currently considered as promising candidates for effective power sources because of their high theoretical efficiency, good availability of ethanol as a fuel, as well as the possibility of obtaining high power densities provided that oxidation of ethanol proceeds according to the 12-electron scheme [1–3]. Ethanol is derived mainly from biomass, it is environmental-friendly, and its use will not impact the CO_2 balance in atmosphere. In practice, there are still many issues to be resolved before DEFC could reach broad commercial market despite recent significant efforts aiming at overcoming the system's limitations [4–14]. The most important problem to be solved is still low practical efficiency of anode and cathode catalysts typically utilizing Pt, Pt/Ru and Pt/Sn nanoparticles [1,2,10,13] and ternary systems containing Pt, SnO_2 and Rh [9,11]. The problem of high cost and practically too low stability of Nafion membranes is also addressed [3,15–19]. It has been recognized that Nafion membranes, being commonly used in PEMFC, are permeable to gases and liquids used as the reactants in PEMFCs [3,15,20–23]. Hydrogen [16,20], methanol [15,21] and ethanol [2,3] crossover has been studied but information about oxygen crossover is scarce, and there is no systematic analysis of

the results of oxygen crossover on efficiency and distribution of products of DEFCs.

Determination of the product distribution of ethanol electrooxidation in a working fuel cell is a key problem when it comes to addressing the catalyst's activity or to optimization of the fuel cell parameters. A high environmental impact of acetaldehyde and acetic acid as main products of ethanol electrooxidation should be mentioned too. Their existence has been quantified and qualified using mainly high performance liquid chromatography (HPLC) [24,25], gas chromatography (GC) [26–28], titration [26,29] and conductometry [22,23]. It is commonly accepted that acetaldehyde, acetic acid, ethyl acetate as well as CO_2 are the main products of ethanol electrooxidation and, in addition to unreacted ethanol, they are present in the mixture leaving anode [24,25]. Obviously the reliable determination of DEFC products is not a trivial task. In the present work, we have utilized GC with mass spectrometry and flame ionization detectors to qualitatively and quantitatively determine the products of ethanol oxidation.

Here we report a systematic analysis of products of ethanol electrooxidation in DEFC where typical anode catalysts such as Pt, Pt/Ru and Pt/Sn have been used. Large amounts of the ethanol oxidation products described above have been detected in a mixture leaving DEFC anode despite operation in current-less mode. This effect would significantly lower efficiency of DEFC, and it shall be attributed to the oxygen permeation phenomenon, which to our best knowledge has not been so far addressed.

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2. Experimental

All chemicals were of analytical grade and were used without further purification. Purity of the ethanol (96%, Pure P.A., POCh, Gliwice, Poland), used to prepare 0.2 mol dm^{-3} ethanol solutions, was confirmed using GC. No contaminations were detected. Acetaldehyde of ACS grade (Sigma–Aldrich) was used to prepare the calibration curve. Deionized water (MiliQ) was utilized in preparation of ethanol solutions. High purity (N5.2) gases (Air Products) were used to deaerate ethanol solutions (Ar) and as a cathode gas (O$_2$). Carbon-supported Pt, Pt/Ru and Pt/Sn nanoparticles (20%), manufactured by ETEK (BASF) on Vulcan XC-72, were used as anode and cathode (Pt) catalysts. 5% Nafion solutions (Sigma–Aldrich) and DuPont Nafion N117 membranes were utilized to prepare the catalysts' suspensions and as fuel cell membranes, respectively.

Products of ethanol oxidation were sampled from the port at the anode outlet, then separated with Hewlett Packard 5890 Series II Gas Chromatograph and, subsequently, detected qualitatively (using Hewlett Packard 5971A Mass Selective Detector – MSD) and quantitatively (using flame ionization detector, FID). FID signal was calibrated from five samples of known amount of acetaldehyde or acetic acid in ethanol (see insets to Fig. 1A and C). Samples for calibration were prepared at −15 °C to reduce volatility of acetaldehyde. The ethanol signal was used as an internal standard. Responses were fitted using linear regression and, in both cases, parameters $R^2 \geq 0.999$ were obtained for acetaldehyde or acetic acid in 0–5 molar percent range (see insets to Fig. 1A and C).

A fuel cell of 10 cm^2 active area, equipped with a single serpentine flow pattern (Fuel Cell Technologies Inc.) was used. Potentials, and current drawn from the fuel cell, were controlled using EG&G Princeton Applied Research 362 Scanning Potentiostat. As a rule, the voltage of fuel cell (tested under load) was not allowed to drop below 300 mV. Following the fuel cell parameter (i.e. voltage/current) change, as a rule the system was stabilized for 30 min before starting the GC product analysis. After the fuel cell temperature change, the system was stabilized for at least 2 h. Fuel was fed using a peristaltic pump at 1 cm^3 min^{-1} rate. O$_2$ flow was monitored using a mass flow controller (Sierra Instruments) at 15 scm^3 s^{-1}, and the backpressure of 200 kPa (29 psi) was maintained.

Fuel cell carbon paper supported electrodes were prepared by appropriate painting with the suspension of a catalyst (in Nafion/ethanol solution) to obtain metal loadings equal to 1.0 mg cm^{-2} (Pt, Pt/Ru or Pt/Sn) for the anode and 1.5 mg cm^{-2} (Pt) for the cathode. Amount of Nafion in a dry catalytic layer was equal to 30% (wt.). After painting, the electrodes were hot pressed at 120 °C and under the pressure of ca. 830 kPa (120 psi).

3. Results and discussion

It was apparent from our preliminary results that use of the ethanol concentration of 0.2 mol dm^{-3} was optimum with respect to the highest currents and the highest acetaldehyde and acetic acid yields observed (relative to ethanol concentration which was used as internal standard). Higher ethanol concentrations would increase maximum power but would decrease the accuracy of quantitative determination of products due to possibility of the chromatographic column overloading. Because most of literature data were reported for higher concentrations, 2 mol dm^{-3} ethanol solutions were also used to characterize the assembled fuel cells. As a rule, reliability and performance of our fuel cell setups was verified with respect to literature [2,13]. Care was exercised to eliminate possibility of short circuiting, oxygen leakage or membrane perforation. We found that Pt/Sn (followed by Pt/Ru and Pt) was the most active anode catalyst towards ethanol electrooxidation, as
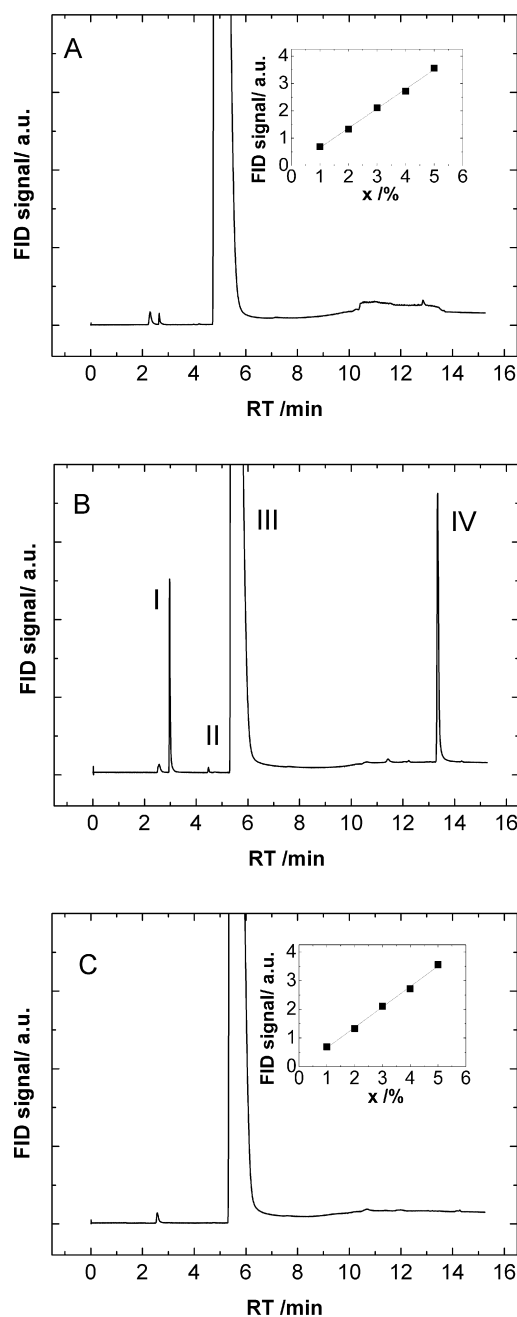

Fig. 1. (A) and (B) Gas chromatograms of a mixture leaving the fuel cell anode under open circuit conditions (anode: Pt/Sn; temperature 80 °C; Nafion N117 is used as a membrane; cathode: Pt). Cathode gases: (A) argon and (B) oxygen at 200 kPa (29 psi). Peaks at 2.9, 4.5, 5.5, and 13.3 min refer to: (I) – acetaldehyde, (II) – ethyl acetate, (III) – ethanol and (IV) – acetic acid, respectively. Peak at 2.5 min is the column dead time. Insets to Fig. 1(A) and (C) show FID calibration curves for acetaldehyde and acetic acid, respectively. Chromatogram A has been registered 60 min after chromatogram B. Chromatogram C is recorded for 0.2 mol dm^{-3} ethanol solution (just before entering the anode compartment). All chromatograms are normalized against the ethanol signal.

reported elsewhere [2,13]. Formation of CO$_2$ was found to be negligible (versus other products), namely less than 5% (molar) for Pt/Sn or Pt/Ru and ca. 15% (molar) in a case of Pt used as anode catalysts. The data were collected under load (current flow), and it was determined from charge balance. No correlation was observed between CO$_2$ yield and oxygen permeation and, therefore, we concentrated on acetaldehyde and acetic acid production.

Analysis of the mixture leaving the anode compartment of the fuel cell shows that, in addition to unreacted ethanol, acetaldehyde, acetic acid and ethyl acetate can be separated using GC and identified using MSD. The most striking feature of the recorded chromatograms (Fig. 1) is the appearance of significant amounts of the ethanol oxidation products in the mixtures leaving anode compartment even under conditions when no current is drawn from the cell (Fig. 1B). We attribute those products to presence of oxygen capable of permeating from cathode compartment through Nafion 117 membrane [20] and parasitically oxidizing ethanol on the surface of anode catalysts. To support this view we have found that the above mentioned products are neither present in the ethanol solution existing just before entering the anode compartment (Fig. 1C) nor in the solution leaving the anode compartment when argon, instead of oxygen, is used as a cathode gas (Fig. 1A).

Increase of ionic conductivity in a mixture leaving anodic compartment of the fuel cell operating under open circuit conditions was reported earlier [22] and attributed to the presence of acetic acid leaching graphite blocks (where it was accumulated during the fuel cell operation) or to its ability to permeate membrane from the cathode compartment. It was postulated [22] that this effect was caused by low-volatility of acetic acid accumulating in the cathode region. Here, we have observed that the amount of acetic acid in the anode stream decreases rapidly upon switching the cathode gas from oxygen to argon. Concentration of acetic acid has decreased more than 1000 times (compare Fig. 1A and B) after 60 min, and it has become completely undetectable after 120 min. The trace amounts of acetaldehyde and acetic acid remaining after 60 min of the argon flow (Fig. 1A) may originate from its accumulation in the porous sponge-like carbon paper (used as a substrate for anode catalysts). While we do not exclude the possibility of permeation of ethanol from the anode to cathode compartment, followed by its oxidation to acetic acid, the subsequent permeation of acetic acid to the anode compartment is of secondary importance under our experimental conditions.
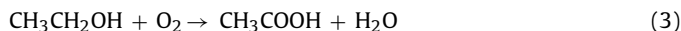
The oxidation processes to acetaldehyde and acetic acid, have the overall schemes [24,30]:

$$CH_3CH_2OH + 1/2O_2 \rightarrow CH_3CHO + H_2O \quad (1)$$
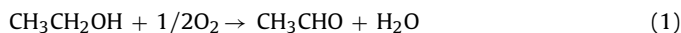
where acetaldehyde can be further oxidized to acetic acid:

$$CH_3CHO + 1/2O_2 \rightarrow CH_3COOH \quad (2)$$

Alternatively, ethanol can be directly oxidized to acetic acid:

$$CH_3CH_2OH + O_2 \rightarrow CH_3COOH + H_2O \quad (3)$$

Thus the oxygen permeation through membrane would severely impact the fuel cell efficiency, since reactions (1)–(3) proceeding in the presence of oxygen do not require the flow of electric current in the external circuit. We define the fuel utilization parameter (N) as follows:

$$N = 100\% \frac{n_{tot} - n_{ocv}}{n_{tot}}$$

where n_{tot} is the total amount of acetaldehyde or acetic acid detected at given potential, and n_{ocv} is the amount detected at open circuit, and other fuel cell parameters (flow rate, temperature etc.) have been kept constant. We have addressed the potential dependence of the N parameter (Fig. 2A–C). When the cell potential becomes higher, current densities tend to be lower and, consequently, the relative formation of products (acetaldehyde and acetic acid) electrochemically is less pronounced. Provided that the real fuel cell should work at potential as high as possible, the oxygen permeation problem becomes sizeable. We have also found (the data for simplicity are not shown here) that higher ethanol concentration will not significantly increase fuel utilization due to the sub-proportional increase of current on concentration. We
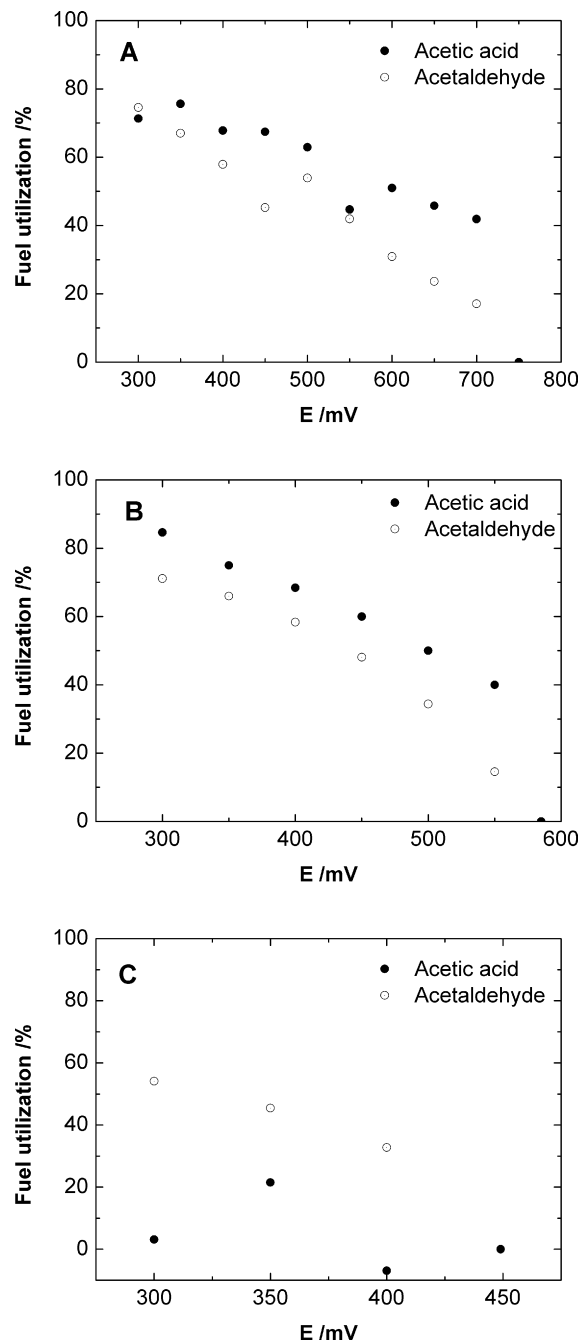

Fig. 2. Dependencies of the fuel utilization parameter on the fuel cell voltage. Anode catalysts: (A) Pt/Sn, (B) Pt/Ru, and (C) Pt. Experimental conditions: $t = 80\,°C$, $0.2\,mol\,dm^{-3}$ ethanol.

determined that following 10-fold increase of concentration from 0.2 to 2 mol dm^{-3} ethanol, current increases only ca. 2.5 times. On the whole, under conditions of the operating fuel cell, oxygen permeating from the cathode compartment parasitically oxidizes at least 20% of the ethanol fuel (Fig. 2). The membrane used here, Nafion 117, is fairly thick (ca. 178 μm), and it is a standard polymer membrane utilized in PEMFCs.

We have considered temperature dependencies of the amounts of acetaldehyde and acetic acid produced under open circuit conditions (Fig. 3). From the data, we can postulate that the catalyst activity is the limiting factor in the parasitic ethanol oxidation. The statement is based on observation about distinct amounts of acetic acid and acetaldehyde produced upon application of different cat-
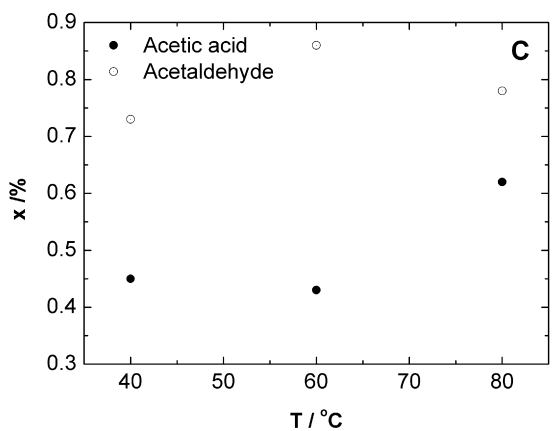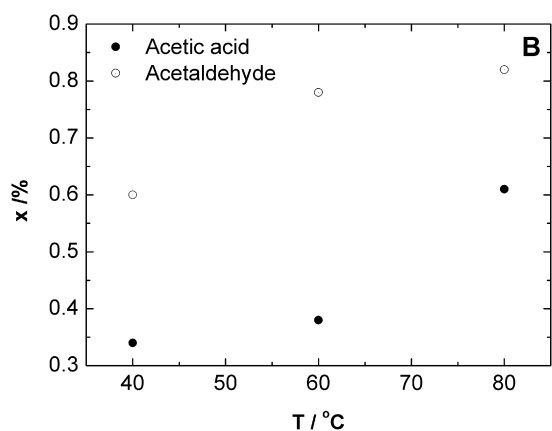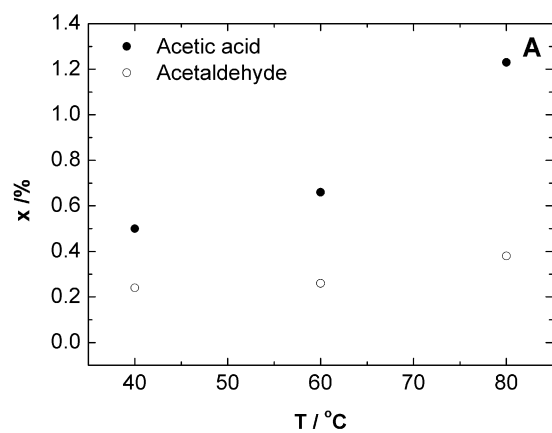
Fig. 3. Percent molar fraction of acetic acid and acetaldehyde in the anode stream from DEFC, recorded under open circuit conditions as a function of temperature. Other conditions as for Fig. 2.

Fig. 4. Percent molar fraction of acetic acid and acetaldehyde in the anode stream from DEFC, recorded under open circuit conditions as a function of oxygen pressure. Other conditions as for Figs. 2 and 3.

Temperature dependencies of the amounts of acetaldehyde and acetic acid produced under open circuit conditions show that the fraction of acetic acid produced increases exponentially with temperature (Fig. 3A–C) whereas the amount of acetaldehyde is almost constant. The latter observation most likely reflects the facts that both reactions (1) and (2), i.e. formation of acetaldehyde and its decomposition to acetic acid, proceed at higher rates.

It was reported that the oxygen mass-flux through Nafion membrane depended linearly on the applied pressure difference [31]. Here we have found that some increases in the acetaldehyde and acetic acid concentrations have been observed as a function of increasing pressure (Fig. 4). It cannot be excluded that, on kinetic grounds, the oxygen permeation rate is comparable to the rate of ethanol electrooxidation at 80 °C. There are many parameters, sole or in combination, affecting dynamics of the parasite ethanol oxidation, and their elucidation will be a subject of future work.

4. Conclusions

We have demonstrated that, in ethanol fuel cell operating under open circuit conditions, oxygen permeating through Nafion 117 membrane from the cathode compartment is responsible for the chemical oxidation of ethanol and formation of large amounts of acetic acid and acetaldehyde in the anode compartment. The existence of this parasitic phenomenon during operation of the fuel cell would result in significant decrease of practical utilization of the fuel. Dynamics of this chemical process is most probably limited by the activity of the catalytic material used. This problem seems to be of general importance to the development of low-temperature fuel cells, and it must be addressed until new improved membranes are developed.

Acknowledgements

References

[1] C. Lamy, E.M. Belgsir, J.M. Leger, Journal of Applied Electrochemistry 31 (2001) 799–809.
[2] F. Vigier, S. Rousseau, C. Coutanceau, J.M. Leger, C. Lamy, Topics in Catalysis 40 (2006) 111–121.
[3] A.S. Arico, S. Srinivasan, V. Antonucci, Fuel Cells 1 (2001) 133–161.

alysts. In particular, for Pt/Sn at 80 °C, ca. 1.23 M% of acetic acid and 0.38 M% of acetaldehyde can be detected (Fig. 3A). To obtain such amounts, and considering the appropriate reaction stoichiometries (Eqs. (1) and (3)), at least 1.42 (1.23 + 1/2(0.38)) molar equivalent of molecular oxygen would be required. Similarly, 0.61 and 0.62 M% of acetic acid and 0.78 and 0.82 M% of acetaldehyde have been detected for Pt/Ru and Pt, respectively (Fig. 3B and C); they require the following molar equivalents of oxygen, 1.02 and 1.01. If the parasitic reaction was limited by oxygen permeation rate, amount of the oxygen used (coming from the cathode compartment) would be the same regardless of the catalyst used. Obviously, this is not the case here.
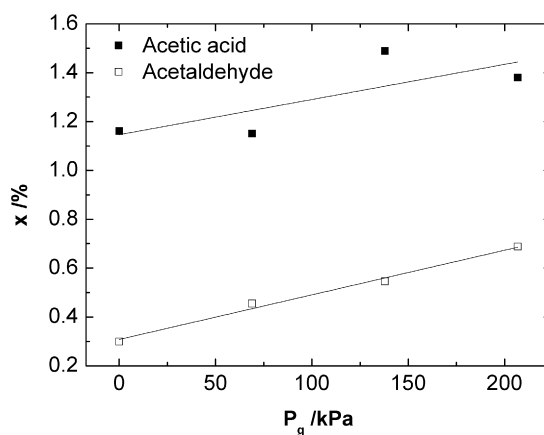
[4] A. Zurowski, A. Kolary-Zurowska, S. Dsoke, P.J. Barczuk, R. Marassi, P.J. Kulesza, Journal of Electroanalytical Chemistry 649 (1–2) (2010) 238–247.
[5] E. Antolini, F. Colmati, E.R. Gonzalez, Journal of Power Sources 193 (2009) 555–561.
[6] F. Colmati, E. Antolini, E.R. Gonzalez, Journal of Solid State Electrochemistry 12 (2008) 591–599.
[7] L. Colmenares, H. Wang, Z. Jusys, L. Jiang, S. Yan, G.Q. Sun, R.J. Behm, Electrochimica Acta 52 (2006) 221–233.
[8] D.M dos Anjos, F. Hahn, J.M. Leger, K.B. Kokoh, G. Tremiliosi, Journal of the Brazilian Chemical Society 19 (2008) 795–802.
[9] A. Kowal, M. Li, M. Shao, K. Sasaki, M.B. Vukmirovic, J. Zhang, N.S. Marinkovic, P. Liu, A.I. Frenkel, R.R. Adzic, Nature Materials 8 (2009) 325–330.
[10] J.M. Leger, S. Rousseau, C. Coutanceau, F. Hahn, C. Lamy, Electrochimica Acta 50 (2005) 5118–5125.
[11] M. Li, A. Kowal, K. Sasaki, N. Marinkovic, D. Su, E. Korach, P. Liu, R.R. Adzic, Electrochimica Acta 55 (2010) 4331–4338.
[12] F.L.S. Purgato, P. Olivi, J.M. Leger, A.R. de Andrade, G. Tremiliosi, E.R. Gonzalez, C. Lamy, K.B. Kokoh, Journal of Electroanalytical Chemistry 628 (2009) 81–89.
[13] P.E. Tsiakaras, Journal of Power Sources 171 (2007) 107–112.
[14] P.J. Barczuk, A. Lewera, K. Miecznikowski, A. Zurowski, P. Kulesza, Journal of Power Sources 195 (2009) 2507–2513.
[15] N.W. Deluca, Y.A. Elabd, Journal of Polymer Science, Part B: Polymer Physics 44 (2006) 2201–2225.
[16] M. Inaba, T. Kinumoto, M. Kiriake, R. Umebayashi, A. Tasaka, Z. Ogumi, Electrochimica Acta 51 (2006) 5746–5753.
[17] A. Pozio, R.F. Silva, M. De Francesco, L. Giorgi, Electrochimica Acta 48 (2003) 1543–1549.
[18] J. Xie, D.L. Wood Iii, K.L. More, P. Atanassov, R.L. Borup, Journal of the Electrochemical Society 152 (2005) A1011–A1020.
[19] J. Xie, D.L. Wood Iii, D.M. Wayne, T.A. Zawodzinski, P. Atanassov, R.L. Borup, Journal of the Electrochemical Society 152 (2005) A104–A113.
[20] S.S. Kocha, J.D. Yang, J.S. Yi, AIChE Journal 52 (2006) 1916–1925.
[21] V. Neburchilov, J. Martin, H. Wang, J. Zhang, Journal of Power Sources 169 (2007) 221–238.
[22] D.D. James, P.G. Pickup, Electrochimica Acta 55 (2010) 3824–3829.
[23] D.D. James, D.V. Bennett, G.C. Li, A. Ghumman, R.J. Helleur, P.G. Pickup, Electrochemistry Communications 11 (2009) 1877–1880.
[24] F. Vigier, C. Coutanceau, F. Hahn, E.M. Belgsir, C. Lamy, Journal of Electroanalytical Chemistry 563 (2004) 81–89.
[25] S. Rousseau, C. Coutanceau, C. Lamy, J.M. Leger, Journal of Power Sources 158 (2006) 18–24.
[26] Q. Wang, G.Q. Sun, L. Cao, L.H. Jiang, G.X. Wang, S.L. Wang, S.H. Yang, Q. Xin, Journal of Power Sources 177 (2008) 142–147.
[27] A.S. Arico, P. Creti, P.L. Antonucci, V. Antonucci, Electrochemical and Solid-State Letters 1 (1998) 66–68.
[28] K. Taneda, T. Taniyama, Y. Yamazaki, Electrochemistry 72 (2004) 700–702.
[29] G. Li, P.G. Pickup, Journal of Power Sources 161 (2006) 256–263.
[30] C. Lamy, A. Lima, V. LeRhun, F. Delime, C. Coutanceau, J.M. Leger, Journal of Power Sources 105 (2002) 283–296.
[31] J.H. Ohs, U. Sauter, S. Maass, D. Stolten, Journal of Power Sources 196 (2011) 255–263.