Short communication

Direct ethylene glycol fuel-cell stack—Study of oxidation intermediate products

V. Livshits, M. Philosoph, E. Peled*

School of Chemistry, Tel-Aviv University, Tel Aviv 69978, Israel

Abstract

In the present paper, a ten 10 cm^2 direct ethylene glycol fuel-cell (DEGFC) stack based on a nanoporous proton-conducting membrane (NP-PCM) is used to study the electro-oxidation of ethylene glycol (EG) in acid medium under initial and steady-state conditions, and under the operating conditions of electrochemical titration. Ethylene glycol (EG) has a theoretical capacity 17% higher than that of methanol in terms of Ah ml^{-1} (4.8 and 4, respectively); this is especially important for portable electronic applications. EG (bp 198 °C) is also a safer fuel for direct-oxidation fuel-cell (DOFC) applications than is methanol. A maximal power of 12 W (at 0.3 V cell^{-1}) at 80 °C has been achieved for a DEGFC fresh stack fed with 0.5 M EG/1.7 M triflic acid solution at ambient dry air pressure. The formation of oxidation by-products – glycolic and oxalic acids (most likely in parallel reactions) – has been proven by ion-chromatography analysis. On continuous feed of EG in order to maintain a concentration of about 0.5 M, the concentration of intermediates reached a maximum after about two fuel (EG) turnovers. After discharging without feeding the stack with EG, there was no further accumulation of these acids and their concentration decreased to almost zero. This is clear evidence that EG is a real fuel that can be converted completely to CO_2.

1. Introduction

Direct methanol fuel cell (DMFC) is a promising electrochemical power generator for a variety of applications. This liquid-feed system is relatively simple, compact and does not require a fuel-processing unit. Therefore, great potential is foreseen in applications including transportation, decentralized power generation and, most importantly, portable devices [1–16]. We recently reported on a high-power (0.5 W cm^{-2}) nanoporous proton-conducting membrane (NP-PCM)-based direct methanol fuel cell (DMFC) operated with triflic acid [17]. The use of the NP-PCM in the DMFC offers several advantages over the Nafion-based DMFC: much lower membrane cost, higher conductivity and lower fuel crossover. Its hydraulic water permeation is more than 10 times that of Nafion 117 [18–22]. Therefore, the water flux through the NP-PCM (to the cathode exhaust) is much smaller, leading to water-neutral operating conditions, reduced cathode–catalyst flooding and low relative humidity in the cathode flow field, and thus to high oxygen partial pressure and improved cell performance [17,22,23]. In addition, the use of the NP-PCM significantly reduces the need for oxidant humidification. The recirculation of the acid-based aqueous electrolyte, which seems to be the main drawback of the NP-PCM-based FC, is also one of its advantages, since, unlike Nafion, the electrolyte can be easily replaced in case of contamination or degradation.

Up to now, methanol (MeOH) has been found to be the best fuel for DOFCs. However, methanol is toxic, highly flammable and has a tendency to pass through the fuel-cell membrane. As a result, in a Nafion-based DMFC, it must be diluted to a concentration of 3–6% before being fed into the cell. Therefore, alternative fuels to MeOH must be considered. A suitable fuel must not be toxic, be safe to handle, and have high energy density. Moreover, it should be oxidized completely to CO_2 with little or no accumulation of oxidation by-products, should have a high boiling point (for use at $T > 100$ °C at near-ambient pressure) and should be commercially available and inexpensive. Ethy-

* Corresponding author. Tel.: +972 3640 8438; fax: +972 3641 4126.
E-mail address: peled@post.tau.ac.il (E. Peled).
URLs: http://www.tau.ac.il/chemistry/peled (E. Peled),
http://www.tau.ac.il/institutes/ifcbc/ (E. Peled).

lene glycol (EG) complies with these requirements. EG has a theoretical capacity 17% higher than that of methanol in terms of $Ah\,ml^{-1}$ (4.8 and 4, respectively), a fact especially important for portable electronic applications. Moreover, it is a more efficient [20,22] and safer (bp 198 °C) fuel for DOFC applications than is methanol. Vielstich et al. studied the electrocatalysis of ethylene glycol oxidation in acidic solution [24] and also included a very good summary of previous publications in this area. They found that on a Pt–Ru catalyst, CO_2, glycolic acid and possibly oxalic acid are formed in parallel reactions. The catalytic activity increases with Ru content, but the complete oxidation of EG to CO_2 is favored by a high Pt content. Recently, a study of the electro-oxidation of a series of polyhydric alcohols in three different electrolytes (H_2SO_4, KOH, and K_2CO_3) on a platinum electrode was reported by Ogumi et al. [25]. EG had the highest reactivity of all the polyhydric alcohols studied and low activity decay in alkaline solutions. Very low EG oxidation to CO_2 (6%) was measured at room temperature with the use of a flow cell [26]. The reason for this low value is the use of a flow cell at room temperature where EG oxidation intermediates are flushed away from the electrodes. As opposed to this, we found very high EG fuel utilization (over 95%), measured in a DEGFC at 80 °C and as low as one-third of the crossover current densities as those for methanol [20,21]. A DEGFC based on a homemade NP-PCM and fed by a sulfuric acid-fuel solution and by dry air delivered $300\,mW\,cm^{-2}$ at 130 °C [27].

The focus of this work is the study of the electro-oxidation intermediate products of ethylene glycol in a 10-cell stack. Our aim was to determine whether there is an accumulation of the intermediates or if they reach a steady-state level. In order to obtain high concentration of these intermediates in a short time, we used a 10-cell stack and a small volume (100 ml) of electrolyte. In addition, we reported on progress in the development of a DEGFC stack and the effect of air starvation on its performance.

2. Experimental

Our test vehicle was a direct ethylene glycol fuel cell (DEGFC) stack comprising ten $10\,cm^2$ cells based on 2.2 mm bipolar plates (Fig. 1). The bipolar plates were built from synthetic graphite blocks (Poco Inc.), in which serpentine flow fields were engraved. The composition of the nanoporous proton-conducting membrane (NP-PCM) was 28% (v/v) poly(vinylidenedifluoride) (PVDF), 12% SiO_2, and 60% pore volume (filled with an acid-fuel solution). It was produced at the Israel Plastics and Rubber Center (IPRC) on a semi-industrial coater (Dixon) at a rate of $15\,m^2\,h^{-1}$. The thickness of the NP-PCM was 100 μm. Two stacks were run: the first (stack 1) was based on Pt–Ru black anode catalyst (1:1 atomic, HiSPEC[TM] 6000, Johnson Matthey) and the second (stack 2) was based on supported Pt–Ru (1:0.7 atomic) anode catalyst (provided by BASF). Both catalyst inks were spread over untefonated Toray paper (at a loading of $5\,mg\,Pt\,cm^{-2}$). The ink contained 2% (w/w) PVDF relative to the catalyst weight. In both stacks, an E-TEK cathode with $5\,mg\,Pt\,cm^{-2}$ was used. The membrane-electrode assemblies (MEAs) were hot-pressed
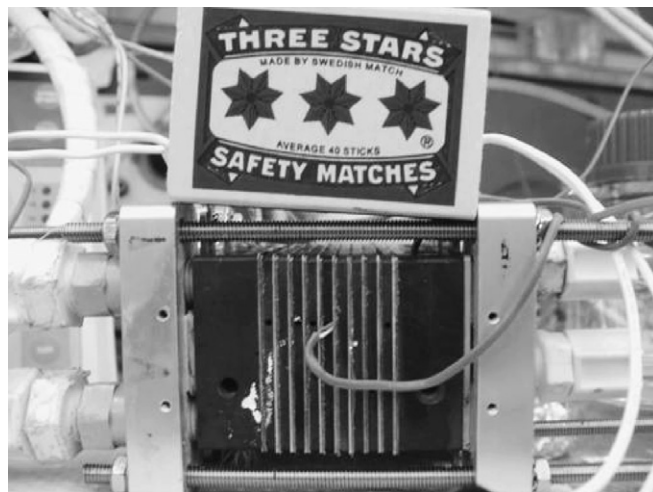

Fig. 1. A 10 ($10\,cm^2$) cell direct ethylene glycol fuel cell (DEGFC) stack.

at 100 °C under a pressure of $24\,kg\,cm^{-2}$. A constant volume (100 ml) of fuel solution, 0.5 M ethylene glycol and 1.7 M triflic acid was circulated in a closed loop over the anode compartments of both stacks. In an additional test, stack 2 was run with a similar fuel solution containing 2 M sulfuric acid (instead of the triflic one), which was circulated in the same manner (we previously found that this range of acid concentrations (1.7–2 M) and the concentration of about 0.5 M of EG were optimal for these tests). Ambient, 2–3 stoich, dry air (room air, not filtered) was fed into the cathode compartments of both stacks. The actual concentration of EG was not measured during the longevity tests. EG was added in order to maintain a concentration of 0.5 M, (which corresponds to a capacity of 13.4 Ah). The cathode condensate was recycled continuously into the anolyte. The stacks were discharged with a Maccor model series 4000 battery tester at a constant voltage of 3 V. Stacks were run continuously at 80 °C and anolyte samples were taken from time to time for ion-chromatography tests. A Dionex DX 500 system with an IonPac AS4A-SC column and ED 40 conductivity detector was used. The injection-loop volume was 20 μl and the electrolyte was 1.8 mM Na_2CO_3/1.7 mM $NaHCO_3$ (fed at $2.0\,ml\,min^{-1}$).

3. Results and discussion

We recently reported on progress achieved in the performance of the direct ethylene glycol fuel cell (DEGFC) following replacement of sulfuric acid by triflic acid and the use of a higher-quality nanoporous proton-conducting membrane (NP-PCM) [27]. Maximal power densities of 45, 80, 285 and $320\,mW\,cm^{-2}$ have been achieved in a fresh, $5\,cm^2$ NP-PCM-based DEGFC under dry-air feed, at 65, 80, 110 and 130 °C, respectively. However, here we publish for the first time the characteristics of a 10-cell stack. As mentioned above, we measured very high fuel efficiency for EG electro-oxidation in "electrochemical (potentiostatic) titration" tests performed at 80 °C [28]. According to these electro-oxidation tests, up to 94% fuel utilization of EG has been achieved. However, in order to prove that EG is a real fuel, it is necessary to show that there is no accumulation of

intermediates during cell operation. In order to collect EG oxidation products efficiently and in a short time, we operated the DEGFC stacks with a constant volume (100 ml) of fuel solution and we also collected and recycled the water from the cathode exhaust back to the anolyte. No significant change in the anolyte volume was observed during this test.

The performance of these stacks was measured starting with discharge at 3 V followed by polarization tests. Stack 2, fed with triflic acid fuel solution delivered very high power – 120 mW cm^{-2} – at the beginning of the discharge ($t = 0$) (Fig. 2a). This dropped to about 65 mW cm^{-2} after 5 min. At $t = 0$, the only organic material in the fuel solution is EG, while during discharge, EG oxidation by-products are formed on both electrodes, (apart from fuel oxidation at the anode, fuel that crosses over to the cathode is oxidized on the Pt-based catalyst). This reduces the activity of both catalysts and leads to lower power. However, for a fresh stack, it is seen from Fig. 2b that this deterioration is, in the short run, reversible: stack performance recovered after 20 s of air starvation (shutting off the air supply) while the OCV of the cell dropped to close to zero. The current spikes in Fig. 2b are caused by these "air starvations". The effect of air starvation was much stronger in the stack based on triflic

acid than it was in the stack based on sulfuric acid. Each "air starvation" increased stack performance, causing it to rebound to the initial value. The relationship between the interruption of oxygen supply and DMFC performance has been recently discussed [29]. We explain this phenomenon as follows: when the oxygen supply is shut down while the fuel solution is circulating, the crossover of fuel from the anode to the cathode continues. Thus, at the cathode, the permeated fuel consumes the oxygen and reduces some of the intermediates that are adsorbed on the platinum-catalyst sites, poisoning them. This reduction results in cleaning these sites and thus leads to performance improvement. The initial power of stack 2 fed with sulfuric acid was about half of that obtained with the triflic acid feed. This results from the deactivation of the platinum catalyst by adsorption of the bisulfate anion. Since the triflate anion does not adsorb on platinum [30], the surface is available for the adsorption of EG and its oxidation by-products.

Stacks 1 and 2 were operated for more than 10 fuel turnovers. The operating conditions were very close to those expected from a fuel cell ($T = 80\,°C$, limited fuel-solution volume, recycling of both the fuel solution and the cathode condensate in a closed loop). Fuel solutions contained mainly EG (Fig. 2a). Stack 2, operated with both types of acid (triflic and sulfuric) showed very uniform voltage distribution among the unit cells (Fig. 3).
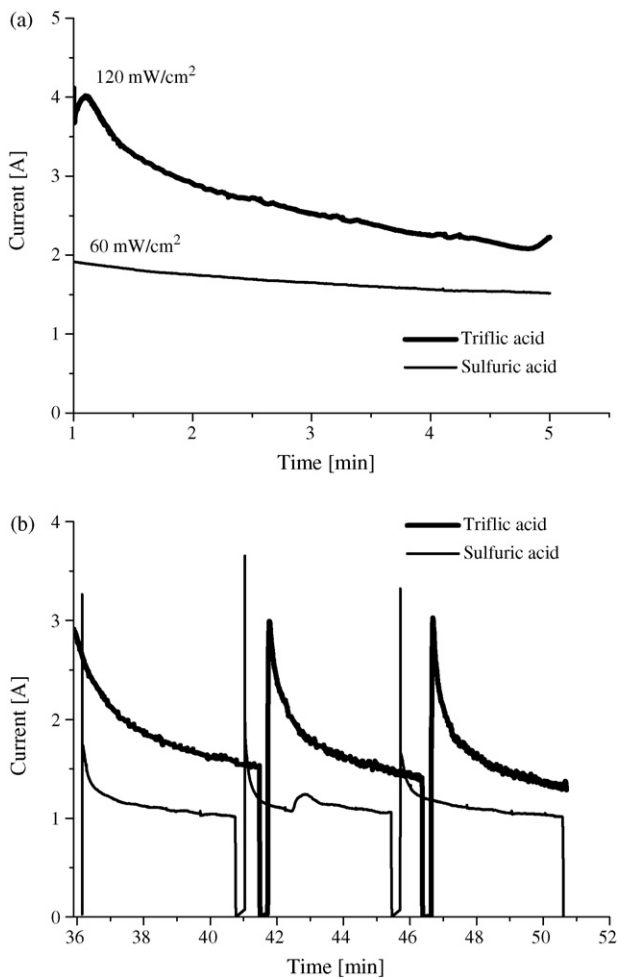

Fig. 2. Comparative performance of stack 2 fed with either triflic- or sulfuric acid-based fuel solutions: (a) initial discharge (fresh stack) and (b) steady-state conditions.
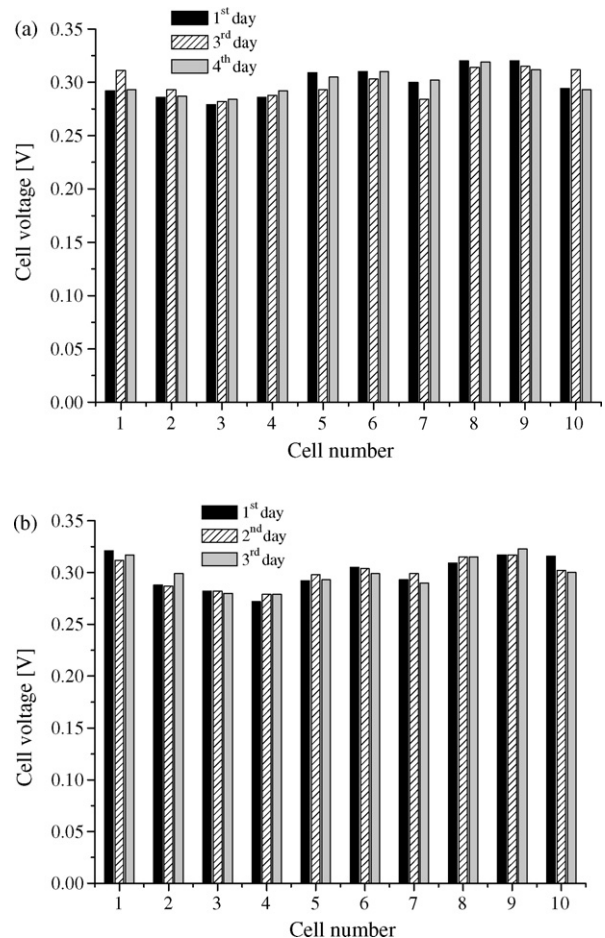

Fig. 3. Cell voltage distribution of stack 2 operated with: (a) 1.7 M triflic acid and (b) 2 M sulfuric acid.
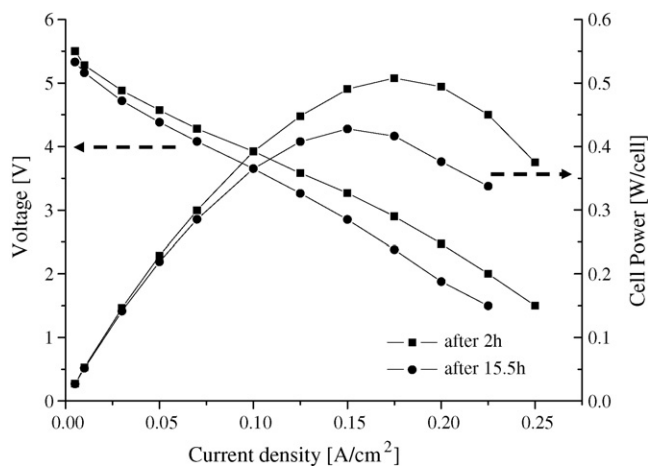
Fig. 4. Stack 2 performance after 2 and 15.5 h of test (triflic acid).

Fig. 6. Time-dependent concentrations of GA and OA in DEGFC stacks. (■) Pt–Ru black (JM), stack 1, 1.7 M triflic acid, GA; (●) BASF Pt–Ru (1:0.7), stack 2, 1.7 M triflic acid, GA; (▲) BASF Pt–Ru (1:0.7), stack 2, 2 M sulfuric acid, GA; (□) Pt–Ru black (JM), stack 1, 1.7 M triflic acid, OA; (○) BASF Pt–Ru (1:0.7), stack 2, 1.7 M triflic acid, OA; (△) BASF Pt–Ru (1:0.7), stack 2, 2 M sulfuric acid, OA.

Furthermore, it exhibited very high initial performance—more than $120 \, mW \, cm^{-2}$ (while fed with the triflic acid-fuel solution) and close to $60 \, mW \, cm^{-2}$ (with the sulfuric acid-fuel solution) at $0.3 \, V \, cell^{-1}$. This difference in stack performance carried on during the whole course of the longevity test.

According to the polarization curves of stack 2 (operating with triflic acid), under steady-state conditions, performance dropped from 50 to $43 \, mW \, cm^{-2}$ after 2 and 15.5 h of operation, respectively (Fig. 4). In the case of the sulfuric acid-based fuel solution, the performance of stack 2 fell from 36 to $27 \, mW \, cm^{-2}$ after 2 and 22.5 h of operation, respectively. These values are similar to those measured in a single DEGFC, in spite of the fact that the stacks in this work were operated under much more difficult test conditions (only 100 ml of acid-fuel solution), than were those of a single cell.

Performance drop of both stacks (regardless of the acid type) is mainly explained by the formation of EG oxidation by-products. At the beginning of the discharge test (fresh EG solution), the oxidation of EG to CO_2 at the Pt–Ru-based anode catalyst is not complete and intermediate oxidation products are being formed. According to the mechanism of stepwise oxidation of EG to CO_2 (Fig. 5), presented by Gonzalez et al. [31],
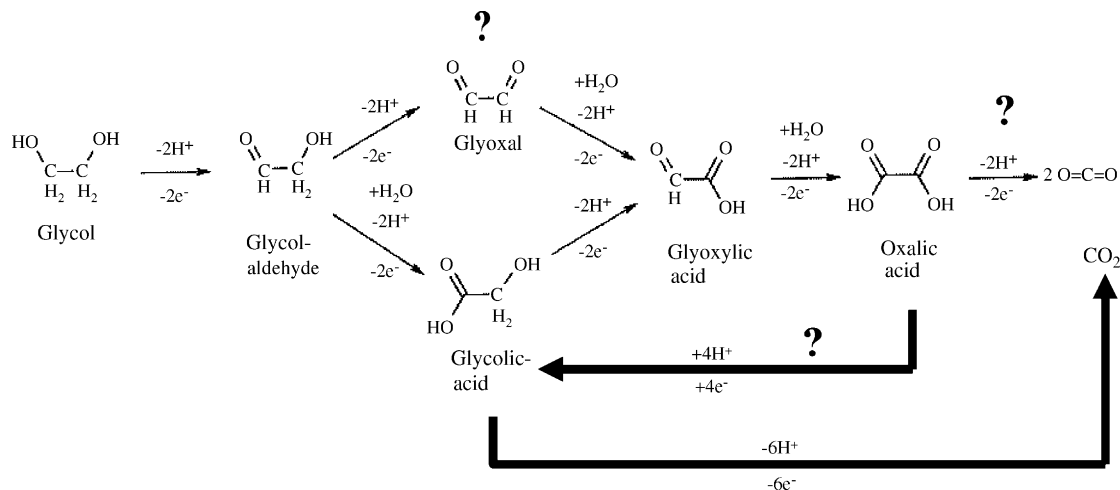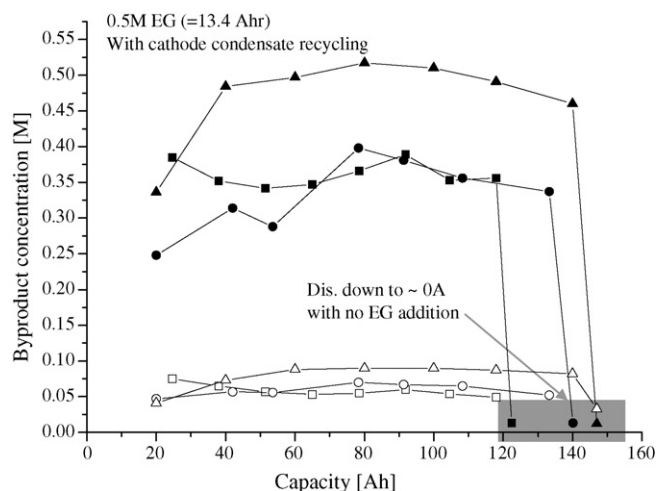
there are several possible intermediates in the conversion of EG to CO_2. In both stacks tested, we found formation of glycolic and oxalic acids (GA and OA, respectively) (Fig. 6). It is worth mentioning that the detection of these intermediates does not contradict the results of the "electrochemical (potentiostatic) titration" test performed previously with the use of a $5 \, cm^2$ single DEGFC [28]. In the latter method, a continuous process of EG oxidation took place (with no further EG addition) until all the oxidizable materials were consumed. In contrast to this, in the DEGFC long-run tests, EG was continuously added to keep its concentration constant at 0.5 M. Since EG is more readily oxidized than its intermediates, the further oxidation of these intermediates is being retarded. As can be seen from Fig. 6, there is no accumulation of GA and OA with time and their concentrations reached a plateau after about two fuel turnovers. In the case of the triflic acid-based fuel solution, the GA concentration reached ∼0.35 M and that of the OA reached ∼0.05 M

Fig. 5. The stepwise oxidation of EG to CO_2.

(in both stacks). These "steady-state" concentrations of GA and OA were higher in case of the sulfuric acid-based fuel solution and reached ~0.5 and 0.09 M for GA and OA, respectively. The concentration of OA is very low in spite of the fact that it is less active than EG or GA [32], and therefore should accumulate. This supports the finding of Kuver and Vielstich [12], suggesting that EG oxidation follows parallel reactions giving rise to CO_2 along with GA as a by-product. We concluded that GA is being directly oxidized to CO_2 without passing through the formation of OA (Fig. 6). Another way to explain this low concentration of OA is the possibility of its reduction back to GA by EG or by another intermediate (so far we have no proof of this path). When discharging the cell without further EG addition, the concentrations of GA and OA fell close to zero (Fig. 6). This finding of no accumulation of GA and OA supports our previous conclusion [27,28] that EG is a real fuel that can be completely oxidized to CO_2.

4. Summary

In this paper we present for the first time the performance achieved in a 10-cell stack DEGFC: $120\,mW\,cm^{-2}$ (at $t = 0$) which dropped to 50 and $43\,mW\,cm^{-2}$ after 2 and 15.5 h of operation in a triflic acid-based fuel solution and $60\,mW\,cm^{-2}$ which decreased to 36 and $27\,mW\,cm^{-2}$ after 2 and 22.5 h of operation in a sulfuric acid-based fuel solution. Using this stack, we found two main by-products in the oxidation of EG – GA and OA. Their concentrations increased during the first two fuel turnovers until they reached steady values. During this experiment, the concentration of EG was kept constant at 0.5 M. After 10 fuel turnovers, a continuous discharge without any EG addition was conducted, at the end of which only minor amounts of GA and OA remained in the fuel solution. These findings, together with the results of the electrochemical (potentiostatic) titration performed previously in our group (demonstrating 94% fuel efficiency for EG) [28], prove that EG is a real fuel and a safe candidate for many fuel-cell applications.

Acknowledgments

References

[1] M. Neerghat, K.A. Friedrich, U. Stimming, in: W. Vielstich, A. Lamm, H.A. Gasteiger (Eds.), Handbook of Fuel Cells, Fundamentals, Technology and Application, vol. 4, no. 6, John Wiley & Sons Ltd., Chichester, 2003, pp. 856–877.

[2] S.R. Narayanan, T.I. Valdez, N. Rohatgi, in: W. Vielstich, A. Lamm, H.A. Gasteiger (Eds.), Handbook of Fuel Cells, Fundamentals, Technology and Application, vol. 3, John Wiley & Sons Ltd., Chichester, 2003, p. 894.

[3] Fuel Cell Handbook, DOE/NETL 2002/1179, 6th ed., 2002.

[4] A.S. Arico, P. Creti, E. Modica, G. Monforte, V. Baglio, V. Antonucci, Electrochim. Acta 45 (2000) 4319.

[5] A.S. Arico, P. Creti, V. Baglio, E. Modica, V. Antonucci, J. Power Sources 91 (2000) 202.

[6] A.S. Arico, S. Srinivasan, V. Antonucci, Fuel Cells 1 (2001) 133.

[7] K. Scott, P. Argyropoulos, K. Sundmacher, J. Electroanal. Chem. 97 (1999) 477.

[8] O. Savadogo, J. New Mater. Electrochem. Syst. 1 (1998) 47.

[9] J. Kerres, W. Zhang, L. Jorissen, V. Gogel, J. New Mater. Electrochem. Syst. 5 (2002).

[10] X.M. Ren, P. Zelenay, S. Thomas, J. Davey, S. Gottesfeld, J. Power Sources 86 (2000) 111.

[11] H. Dohle, H. Schmitz, T. Bewer, J. Mergel, D. Stolten, J. Power Sources 106 (2002) 313.

[12] A. Kuver, W. Vielstich, J. Power Sources 74 (1998) 211.

[13] S.R. Narayanan, T. Valdez, N. Rohatgi, J. Christiansen, W. Chun, G. Voecks, G. Halpert, in: S. Gottesfeld, T.F. Fuller (Eds.), Proton Conducting Membrane Fuel Cells II, The Electrochemical Society Proceedings Series, PV 98-27, The Electrochemical Society, Pennington, NJ, 1999, p. 316.

[14] A.S. Arico, V. Baglio, A.D. Blasi, E. Modica, P.L. Antonucci, V. Antonucci, J. Electroanal. Chem. 557 (2003) 167.

[15] V. Gogel, T. Frey, Z. Yongsheg, K.A. Friedrich, L. Jorissen, J. Garche, J. Power Sources 127 (2004) 172.

[16] M. Kunimatsu, T. Shudo, Y. Nakajima, JSAE Rev. 23 (2002) 21.

[17] E. Peled, V. Livshits, M. Rakhman, A. Aharon, T. Duvdevani, M. Philosoph, T. Feiglin, Electrochem. Solid-State Lett. 7 (12) (2004) 507–510.

[18] E. Peled, T. Duvdevani, A. Melman, Electrochem. Solid-State Lett. 1 (5) (1998) 210.

[19] E. Peled, T. Duvdevani, A. Aharon, A. Melman, Electrochem. Solid-State Lett. 3 (12) (2000) 525.

[20] E. Peled, T. Duvdevani, A. Aharon, A. Melman, Electrochem. Solid-State Lett. 4 (4) (2001) 38–41.

[21] E. Peled, V. Livshits, T. Duvdevani, J. Power Sources 106 (2002) 245.

[22] A. Blum, T. Duvdevani, M. Philosoph, N. Rudoy, E. Peled, J. Power Sources 117 (2003) 22.

[23] E. Peled, A. Blum, A. Aharon, M. Philosoph, Y. Lavi, Electrochem. Solid-State Lett. 6 (12) (2003) A268.

[24] R.B. de Lima, V. Paganin, T. Iwasita, W. Vielstich, Electrochim. Acta 49 (2003) 85–91.

[25] Z. Ogumi, et al., Proceedings of the 204th ECS Meeting (Abs. 1070), 2003.

[26] H. Wang, Y. Zhao, Z. Jusys, R.J. Behm, J. Power Sources (2005).

[27] V. Livshits, E. Peled, J. Power Sources 161 (2006) 1187–1191.

[28] E. Peled, T. Duvdevani, A. Aharon, A. Melman, Electrochem. Solid-State Lett. 4 (4) (2001) A38–A41.

[29] S. Reichman, A. Ulus, E. Peled, J. Electrochem. Soc. 154 (3) (2007) b327.

[30] N.M. Markovic, T.J. Schmidt, V. Stamenkovic, P.N. Ross, Fuel cells 1 (2) (2001) 105.

[31] M.J. Gonzales, C.T. Hable, M.S. Wrighton, J. Phys. Chem. B 102 (1998) 9881–9890.

[32] V. Livshits, M. Philosoph, E. Peled, Polymer Batteries—Fuel Cell Conference, Rome, June 11–14, 2007.