



Short communication

## Passive DMFCs with PtRu catalyst on poly(3,4-ethylenedioxythiophene)-polystyrene-4-sulphonate support

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## ABSTRACT

Passive direct methanol fuel cells (DMFCs) are considered interesting candidates for small-scale power applications. We investigated the performance in passive DMFCs of the PtRu catalyst supported on poly(3,4-ethylenedioxythiophene)-polystyrene-4-sulphonate (pEDOT-pSS), a Nafion<sup>®</sup>-free, mixed electronic–protonic conductor that assures electronic transport for methanol oxidation at the anode and provides the proton movement. The DMFCs were assembled with Vulcan XC-72R carbon/Pt (in excess) cathode, Nafion<sup>®</sup> 117 membranes and 1 M CH<sub>3</sub>OH, and long-time performance data are reported and discussed.

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### 1. Introduction

Air-breathing direct methanol fuel cells (DMFCs), also called passive DMFCs, are considered interesting candidates for small portable devices requiring miniaturization and power from 100 mW to 3 W, and the most important companies in the field of mobile devices already have prototypes powered by these DMFCs [1,2].

Passive DMFCs usually need large amounts of catalysts, even 10 times higher than active DMFCs, which in turn require higher values than those of H<sub>2</sub> fed fuel cells. Unlike active DMFCs, assembled with the PtRu and Pt catalysts supported on carbon [3] for the anode and the cathode, many passive DMFCs operate with unsupported catalysts deposited on the Nafion<sup>®</sup> membrane [4,5] or on gas diffusion layers [6–9]; passive cells with carbon supported catalysts are also under study [5,6,10–13]. The optimum catalyst loading mainly depends on the characteristic of the complete assembly, including type of catalyst, Nafion<sup>®</sup> membrane and CH<sub>3</sub>OH concentration. While very high unsupported catalyst loadings up to 8–12 mg cm<sup>−2</sup> were used both for PtRu and Pt [7,9,14], for supported PtRu and Pt catalysts a loading of 2.5 mg cm<sup>−2</sup> has been indicated as the best performing [10]. The effect of methanol concentration and membrane thickness in passive DMFCs has been investigated and the performance of passive DMFCs fed by a very concentrated CH<sub>3</sub>OH solution, up to 20 M, by CH<sub>3</sub>OH vapor or by neat liquid CH<sub>3</sub>OH are

reported [6,14–18]. The thickness of the Nafion<sup>®</sup> membrane and the CH<sub>3</sub>OH concentration affect methanol crossover and, in turn, DMFC internal temperature. Indeed, methanol crosses the membrane by diffusion and by electro-osmotic transport from the anode to the cathode and chemically reacts with oxygen. This results in decreased fuel utilization, a mixed potential leading to a sharp drop in cathode voltage, and direct combustion of methanol at the cathode that increases the DMFC's internal temperature. High membrane thickness and low methanol concentration reduce the crossover rate and the related detrimental effects. Air, water and temperature management [8,19], CO<sub>2</sub> release [19] and electrode architecture [5,20–22] are also of paramount importance in cell performance.

Given the renewed interest in conducting polymers as an alternative to carbon supports [23–30], we recently demonstrated [23] the viability of pEDOT-pSS, a mixed electronic–protonic conductor, as a Nafion<sup>®</sup>-free support for PtRu in DMFCs. We now report performance data over long operational times of passive DMFCs with supported catalysts, PtRu on pEDOT-pSS for the anode and Pt (in excess with respect to Pt in PtRu catalyst) on Vulcan XC72-R carbon for the cathode, assembled with Nafion<sup>®</sup> 117 membrane and 1 M CH<sub>3</sub>OH. The performance data of the passive DMFCs with PtRu supported on Vulcan carbon are also reported for comparison.

### 2. Experimental

The chemical synthesis of pEDOT-pSS was carried out at room temperature in aqueous solutions (MQ water, 18.2 MΩ cm, from Millipore Simplicity 185) with 1:1 EDOT (Aldrich, 99.7%): SS (from

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**Table 1**  
Catalytic activity of passive DMFCs at RT with 1 M CH<sub>3</sub>OH solution and Nafion 117

DMFC	Anode loading mg cm <sup>-2</sup>	Pt in PtRu mg cm <sup>-2</sup>	Cathode loading mg cm <sup>-2</sup>	Pt mg cm <sup>-2</sup>	$R_{+/-}$	$I_{max}$		$P_{max}$		Sprayed Nafion % anode loading
						mA cm <sup>-2</sup>	$A_{g_{anode}} Pt^{-1}$	mW cm <sup>-2</sup>	$W_{g_{anode}} Pt^{-1}$	
pEDOT-pSS/PtRu										
A	4.36	1.18	8.33	2.50	2.1	2.79	2.37	0.42	0.36	5.4
B	4.99	1.35	9.22	2.83	2.1	2.68	1.99	0.40	0.30	1.9
Vulcan/PtRu										
C	9.04	1.46	8.78	2.81	1.9	1.55	1.06	0.27	0.19	2.7
D	9.26	1.50	9.61	3.07	2.1	1.48	0.99	0.26	0.17	2.6

NapSS, Aldrich MW = 70,000) molar ratio using Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Fluka, >98%) as oxidant in a 10:1 ratio with the monomer. The PtRu (1:1) was chemically deposited on pEDOT-pSS ball-milled powder and on Vulcan XC-72R commercial carbon as in refs. [23,13]. The Pt contents of pEDOT-pSS/PtRu and Vulcan/PtRu were 27 and 16 wt.%, respectively, as experimentally determined after mineralization of the powders by the tin (II) chloride colorimetric method [31]. The deposition of Pt was performed on Vulcan carbon as in ref. [32] and 30 wt.% Pt loading was experimentally determined.

The anodes were prepared by spraying the two 2-propanol-based inks containing pEDOT-pSS/PtRu and Vulcan/PtRu onto 4 cm<sup>2</sup> carbon paper (CP) substrates (Hydro2Power, Italy, 0.3 mm), the former ink being prepared without Nafion<sup>®</sup> and the latter with 20% of Nafion<sup>®</sup>. For the cathodes, Vulcan/Pt-based ink with 20% Nafion was sprayed on teflonized CP (Hydro2Power, Italy, 0.3 mm) substrates.

Passive DMFCs fueled with 1 M CH<sub>3</sub>OH solution were built with pEDOT-pSS/PtRu or Vulcan/PtRu anodes and Vulcan/Pt cathodes hot-pressed onto a Nafion<sup>®</sup> 117 (Hydro2Power, Italy). A small amount of a 1 wt.% of Nafion<sup>®</sup> solution in water was sprayed on top of the electrodes for better adhesion just before hot-pressing them onto the Nafion<sup>®</sup> membrane, which had been treated in 3% H<sub>2</sub>O<sub>2</sub>, in water, in 0.5 M H<sub>2</sub>SO<sub>4</sub> and again in water for 1 h at 80 °C in turn before use. The amount of the sprayed Nafion<sup>®</sup>, as evaluated by weighing of sacrificial electrodes, was 0.25 mg cm<sup>-2</sup> and in one case 0.1 mg cm<sup>-2</sup> (B-DMFC). The cells were held together by two acrylic plates with fixed stainless steel current collectors; the CH<sub>3</sub>OH solution was placed in a reservoir built in the anode plate and the oxygen diffused into the cathode through the openings of the cathode plate to air. The DMFC reservoir (1.7 mL) was filled with 1 M CH<sub>3</sub>OH. The DMFCs were tested at room temperature (RT) by short-time and prolonged-time tests. The former were chronoamperometry tests at different cell potentials (60 s at each potential) to build the current-power plots and the latter were chronopotentiometry tests at constant current for several hours or galvanostatic continuous steps (more than 1000) during which the cell remained 120 s at open circuit (off-state) and 60 s at different constant currents (on-state). These tests were repeated several times after refreshing the CH<sub>3</sub>OH solution in the reservoir and fresh fuel was used for checking the status of the DMFCs after testing.

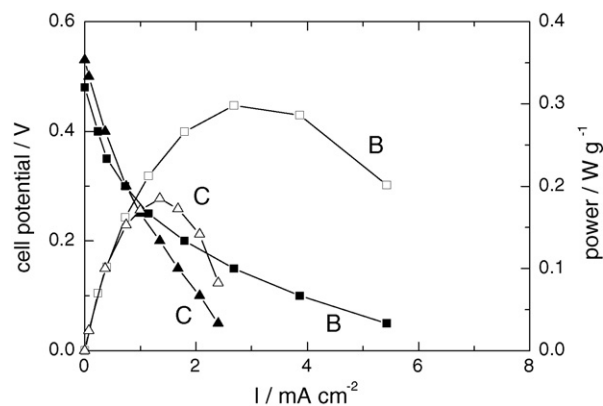
All electrochemical measurements were performed with a multichannel potentiostat/galvanostat PAR VMP. The potentials of the electrodes were evaluated with an Ag quasi reference electrode, that was placed into a hole of the CH<sub>3</sub>OH reservoir, whose potential was measured vs. a saturated calomel electrode before each set of measurements; all the values were recalculated vs. standard hydrogen electrode (SHE). The current and power densities were evaluated by taking into account that the effective area in contact with the CH<sub>3</sub>OH solution was 3 cm<sup>2</sup>; the specific current and power were calculated only by considering the weight of the Pt in the PtRu at the anode given that all the DMFCs were assembled with catalyst at the cathode in excess (roughly double in weight).

### 3. Results and discussion

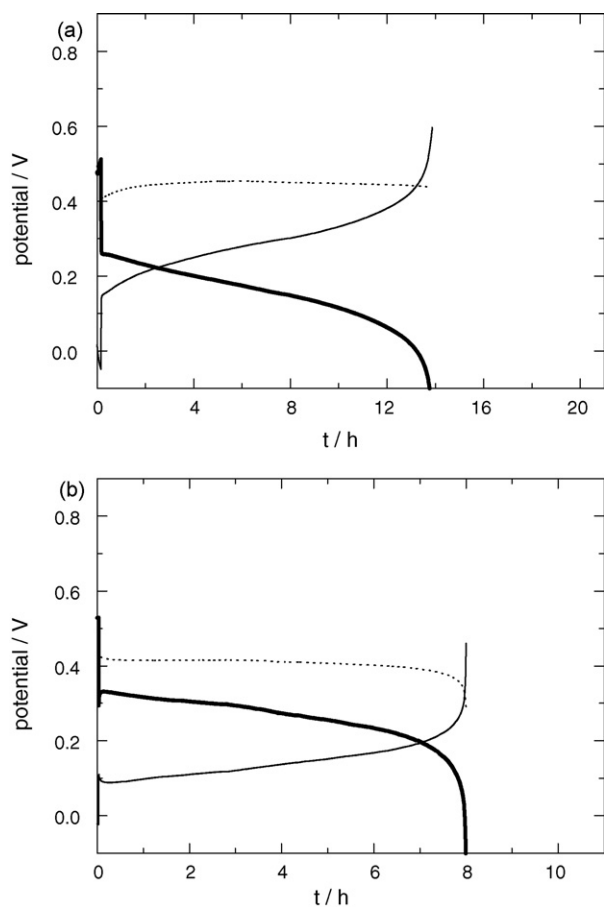
All the passive DMFCs first underwent potentiostatic tests (60 s at each potential) at RT to evaluate their initial performance in terms of maximum current and power density and maximum specific current and power ( $I_{max}$  and  $P_{max}$ ), and some data are shown in Table 1 and Fig. 1. The type and Pt content of selected anodes and cathodes used in the passive DMFCs and the ratio ( $R_{+/-}$ ) of the Pt content of the cathode catalyst to the anode PtRu (1:1) catalyst are reported in the table, which also shows the Nafion<sup>®</sup> percentages (as dry ionomer) sprayed, for a better electrode/membrane adhesion, on the top of the electrodes with respect to the anode loading; the same amount of Nafion<sup>®</sup> was also sprayed on the top of the corresponding cathode. The  $R_{+/-}$  values suggest that the DMFCs operated under non-limited cathode conditions so that their performance should be mainly affected by those of the anodes. Fig. 1 shows the plots of the cell potential and specific power vs. current density of the B- and C-DMFCs, which were assembled with electrodes having comparable Pt loadings.

Although for both types of DMFC cells the  $I_{max}$  and  $P_{max}$  values are not high per se, they indicate that pEDOT-pSS/PtRu performs even better than the conventional Vulcan carbon/PtRu. The obtained  $P_{max}$  values reflect the simple hand-made cell assembly where the components of commercial demonstrative cells, such as stainless steel current collectors, gaskets and end-plates, were adapted and it is well known that optimized, tailor-made components greatly improves the performance of the DMFCs [5,11,12].

All the DMFCs with pEDOT-pSS/PtRu anode then underwent prolonged-time tests by applying constant currents for several hours to evaluate their performance and durability over long working periods, tailoring the test time to the amount of methanol in the reservoir; the potential of the electrodes was also monitored then (while the potential values could be affected by the position



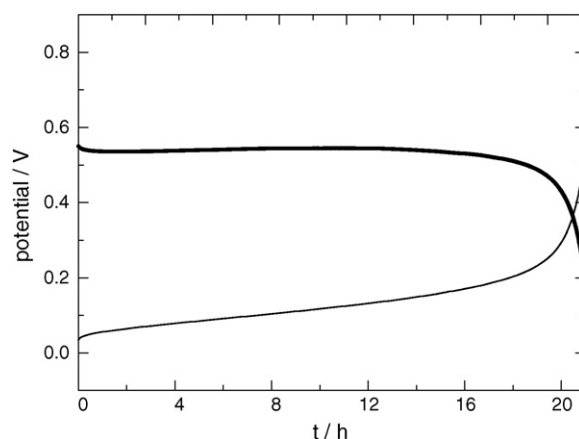
**Fig. 1.**  $I$ - $V$  (solid symbols) and  $I$ - $P$  (plain symbols) characteristics at RT of (B) pEDOT-pSS/PtRu (1.35 mg<sub>Pt</sub> cm<sup>-2</sup>)/Nafion<sup>®</sup> 117/Pt (2.83 mg<sub>Pt</sub> cm<sup>-2</sup>)/Vulcan and (C) Vulcan/PtRu (1.46 mg<sub>Pt</sub> cm<sup>-2</sup>)/Nafion<sup>®</sup> 117/Pt (2.81 mg<sub>Pt</sub> cm<sup>-2</sup>)/Vulcan passive DMFCs.



**Fig. 2.** DMFC (thick solid line), anode (thin solid line) and cathode (dotted line) potential profiles of A-DMFC with pEDOT-pS/PtRu ( $\text{Pt} = 1.18 \text{ mg cm}^{-2}$ ) and Vulcan/Pt ( $\text{Pt} = 2.50 \text{ mg cm}^{-2}$ ) at (a)  $1 \text{ mA cm}^{-2}$  and (b)  $2 \text{ mA cm}^{-2}$  after fuel renewed. The electrode potentials are vs. SHE.

of the Ag quasi reference electrode in the reservoir, their variations throughout the test are of interest).

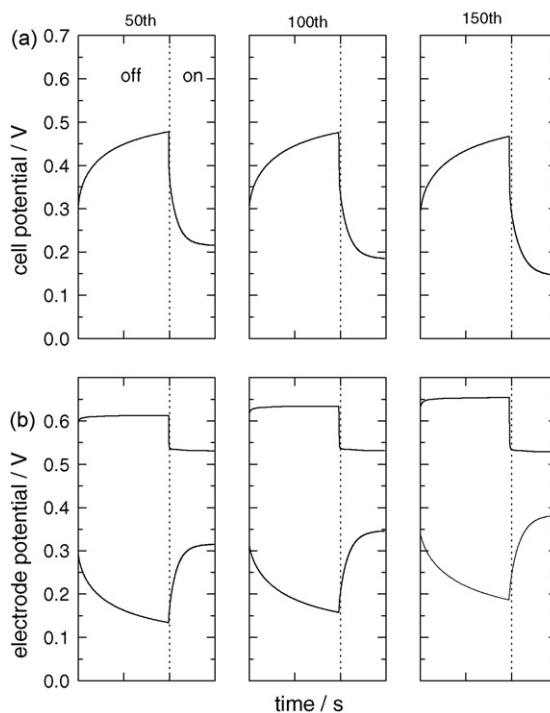
Fig. 2a shows the cell and electrode voltage profiles of the A-DMFC with pEDOT-pS/PtRu ( $\text{Pt} = 1.18 \text{ mg cm}^{-2}$ ) and Vulcan/Pt ( $\text{Pt} = 2.50 \text{ mg cm}^{-2}$ ) under ca. 13 h-working time at  $1 \text{ mA cm}^{-2}$ . The open circuit voltage (OCV) before this galvanostatic test was ca. 0.5 V, a value not far from those reported in literature for passive DMFCs. While the anode potential was ca. 0 V, the cathode potential was ca. 0.5 V and its high deviation from the thermodynamic value is a consequence of the methanol crossover process, which leads to a mixed potential. Under current flow, while the cathode potential with catalyst in excess remained almost constant near 0.4 V vs. SHE, the anode potential gradually increased, from 0.15 V vs. SHE up to an abrupt spike, thus determining the sharp decrease of cell potential after ca. 13 h. The rate of decrease in cell potential, higher than that for active DMFCs [33], is mainly due to the fact that the oxidation reaction at the anode becomes controlled by the methanol concentration in the reservoir, which contains only 1.7 mL of 1 M  $\text{CH}_3\text{OH}$ , as demonstrated by the recovery of cell performance after fuel renewal. Fig. 2b shows that after addition of new methanol solution the DMFC recovers its initial OCV and still works over 8 h at a double current,  $2 \text{ mA cm}^{-2}$ , before the sharp potential decrease. The formation of  $\text{CO}_2$  at the anode and accumulation of water at the cathode, which hinders access to the air, also play a role in cell potential decrease, as does methanol crossover. Given that the cell voltage decrease was ca.  $15 \text{ mV h}^{-1}$  over the first 6 h at  $1 \text{ mA cm}^{-2}$  and only ca.  $12 \text{ mV h}^{-1}$  over the first 3 h at  $2 \text{ mA cm}^{-2}$ , at equal flowed charge, it means that methanol crossover plays a



**Fig. 3.** Cell (thick solid line) and anode (thin solid line) potential profiles of A-DMFC with pEDOT-pS/PtRu ( $\text{Pt} = 1.18 \text{ mg cm}^{-2}$ )/Nafion 117/Pt ( $\text{Pt} = 2.50 \text{ mg cm}^{-2}$ )/Vulcan during open circuit conditions. The anode potential is vs. SHE.

more important part in potential decrease when current flow is lower. Lower currents consume less methanol at the electrode and it is reasonable that a higher amount of fuel crosses the Nafion® membrane. This is confirmed by the results in Fig. 3, displaying the cell and anode potential profiles in open circuit conditions over several hours for the DMFC with new methanol solution. After ca. 21 h the cell potential sharply decreased to 0.2 V, the anode potential increasing by ca. 350 mV for the decreased concentration of the methanol in the reservoir because of the crossover.

We also performed continuous galvanostatic steps on the same DMFC with renewed fuel; in each step a constant current was applied for 60 s to the cell after a period of 120 s in open circuit conditions. Fig. 4 shows the cell and electrode OCV profiles and those under current flow of  $1 \text{ mA cm}^{-2}$  at different number of steps.



**Fig. 4.** 50th, 100th and 150th steps of A-DMFC with pEDOT-pSS/PtRu ( $1.18 \text{ mg cm}^{-2}$ )/Nafion 117/Pt ( $2.50 \text{ mg cm}^{-2}$ )/Vulcan at RT: (a) cell potential profiles and (b) electrode potential profiles vs. SHE during the off-state (OCV) and the on-state ( $1 \text{ mA cm}^{-2}$  current applied).

**Table 2**  
Cell and electrode potentials in open circuit (off-state) and under different current densities (on-state) of A-DMFC at RT

	On-state current				
	1 mA cm <sup>-2</sup>	2 mA cm <sup>-2</sup>	3 mA cm <sup>-2</sup>	4 mA cm <sup>-2</sup>	5 mA cm <sup>-2</sup>
Off-state potential					
Cell/V	0.589	0.604	0.616	0.624	0.634
Cathode/V	0.588	0.594	0.600	0.602	0.610
Anode/V	-0.001	-0.010	-0.016	-0.022	-0.024
On-state potential					
Cell/V	0.378	0.307	0.250	0.203	0.160
Cathode/V	0.530	0.485	0.442	0.406	0.373
Anode/V	0.152	0.178	0.192	0.203	0.213

The electrode potentials are vs. SHE.

During these tests, the methanol crossover becomes more influential than during tests under continuous current because discontinuous fuel consumption makes it possible for non-reacted methanol to cross the membrane. Indeed, Fig. 4 shows that after 150 steps there is the same decrease in cell potential in on-state as there is after 8 h of continuous current flux at the same current (it took 7.5 h to complete 150 steps but the current flowed for only one-third of the time). The Figure also shows the slow recovery of potential values in open circuit conditions.

Galvanostatic tests on the same passive DMFC continued for more than 1200 steps, varying the current density; the methanol solution was renewed after each sequence of ca. 150 steps and the status of the passive cell was checked from time to time by building the power vs. current plots by potentiostatic measurements. Table 2 has the cell and electrode potentials in open circuit and under current recorded at the end of the off- and of the on-state of the step 10, 20, 30, 40 and 50 of a 50-step sequence performed at 1, 2, 3, 4 and 5 mA cm<sup>-2</sup> (10 steps each current value) after 1200 steps were completed. As expected cell voltage decreased with increas-

ing current value. However, the potential of the anode increased only by ca. 60 mV for an increase of the current density from 1 to 5 mA cm<sup>-2</sup>, thus demonstrating the good catalytic performance of PtRu on the Nafion®-free pEDOT-pSS support. It is also worth noting that the OCV values of the cell after long working time are higher (around 0.6 V) than those measured just after assembly or after short working time. On the other hand, the plots of voltage and power density vs. current density, evaluated after a different number of steps (with renewed methanol solution), clearly evinced an enhancement of DMFC performance over time, as shown in Fig. 5 where the *I*-*V* and *I*-*P* characteristics of the A-DMFC are reported.

After 1000 steps the *P*<sub>max</sub> and *I*<sub>max</sub> values were almost double those after 150 steps. This enhancement is not surprising because it has already been reported that discharges at high current densities are beneficial for the functioning of the MEA [6,12,17]. Sequence of tests for an operating time of more than 100 h, like those reported above, were carried out on several passive DMFCs with pEDOT-pSS/PtRu anode where the Pt content ranged from 1.2 to 1.4 mg cm<sup>-2</sup> and all the DMFCs performed similarly to A cell (for example, after 1000 steps the B-cell reached 0.8 mW cm<sup>-2</sup>), demonstrating the effectiveness of Nafion®-free pEDOT-pSS support for PtRu catalytic system and the limiting effect of methanol crossover on the overall performance of the cells.

#### 4. Conclusions

The comparison of non-optimized passive DMFCs with PtRu supported on pEDOT-pSS and on Vulcan carbon clearly indicated that the *P*<sub>max</sub> and *I*<sub>max</sub> values are even better when the catalyst is supported on pEDOT-pSS rather than on Vulcan carbon, thus demonstrating that the protonic properties of pEDOT-pSS are adequate for its use as Nafion®-free support for PtRu catalytic layer for methanol oxidation.

The long-time operating tests, with duration tailored to reservoir volume and to methanol concentration, of the passive DMFCs with pEDOT-pSS/PtRu indicate that the maximum operating time of these cells is mainly limited by methanol crossover, which notably contributes to the decrease of fuel supply as the cells completely recovered their catalytic activity when the reservoir was refreshed with new methanol solution. Methanol crossover also brings about the mixed potential at the cathode that is responsible for the low DMFC potentials.

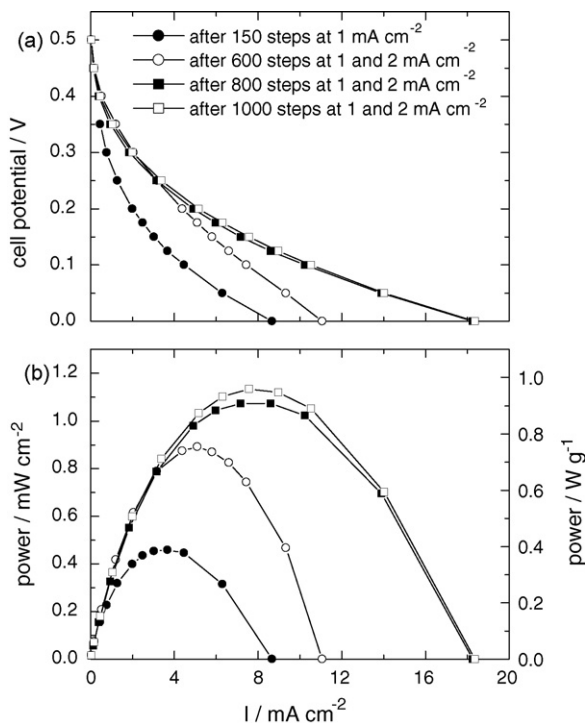
The *P*<sub>max</sub> and *I*<sub>max</sub> values at RT (the best are those of A-DMFC, 1.1 mW cm<sup>-2</sup> and 7.6 mA cm<sup>-2</sup>) of the DMFCs with pEDOT-pSS/PtRu anodes evaluated after more than 100-operating hours with renewed methanol solution show the good long-lasting performance of the pEDOT-pSS/PtRu catalytic system. To our knowledge this is the first time that a mixed conductive polymer support for PtRu, alternative to carbon, has been proved over long operational times in DMFCs. Work is in progress on passive DMFCs with the pEDOT-pSS/PtRu catalytic system at the anode and with new protonic membranes to limit methanol crossover.

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#### References

- [1] S.K. Kamarudin, W.R.W. Daud, S.L. Ho, U.A. Hasran, J. Power Sources 163 (2007) 743–754.
- [2] [www.fuelcelltoday.com/FuelCellToday/FCTFiles/FCTArticleFiles/Article\\_1141\\_Portable%202006%20Survey.pdf](http://www.fuelcelltoday.com/FuelCellToday/FCTFiles/FCTArticleFiles/Article_1141_Portable%202006%20Survey.pdf).
- [3] H. Liu, C. Song, L. Zhang, J. Zhang, H. Wang, D.P. Wilkinson, J. Power Sources 155 (2006) 95–110.



**Fig. 5.** *I*-*V* (a) and *I*-*P* (b) characteristics at RT of A-DMFC with pEDOT-pSS/PtRu (1.18 mg<sub>Pt</sub> cm<sup>-2</sup>)/Nafion® 117/Pt (2.50 mg<sub>Pt</sub> cm<sup>-2</sup>)/Vulcan. The cell performed 400 steps at 1 mA cm<sup>-2</sup>, 600 steps at 2 mA cm<sup>-2</sup> and 250 steps at different currents, intercalated by galvanostatic tests at 1 mA cm<sup>-2</sup> for 14 h and 2 mA cm<sup>-2</sup> for 8 h.

- [4] K.-C. Yu, W.-J. Kim, C.-H. Chung, J. Power Sources 163 (2006) 34–40.
- [5] W.M. Yang, S.K. Chou, S. Shu, J. Power Sources 164 (2007) 549–554.
- [6] J.G. Liu, T.S. Zhao, R. Chen, C.W. Wong, Electrochem. Commun. 7 (2005) 288–294.
- [7] B. Bae, B.K. Kho, T.-H. Lim, I.-H. Oh, S.-A. Hong, H.Y. Ha, J. Power Sources 158 (2006) 1256–1261.
- [8] G. Jewett, Z. Guo, A. Faghri, J. Power Sources 168 (2007) 434–446.
- [9] M.A. Abdelkareem, N. Nakagawa, J. Power Sources 165 (2007) 685–691.
- [10] T. Shimizu, T. Momma, M. Mohamedi, T. Osaka, S. Sarangapani, J. Power Sources 137 (2004) 277–283.
- [11] C.Y. Chen, P. Yang, J. Power Sources 123 (2003) 37–42.
- [12] J.J. Martin, W. Qian, H. Wang, V. Neburchilov, J. Zhang, D.P. Wilkinson, Z. Chang, J. Power Sources 164 (2007) 287–292.
- [13] C. Arbizzani, S. Beninati, E. Manferrari, F. Soavi, M. Mastragostino, J. Power Sources 172 (2007) 578–586.
- [14] M.A. Abdelkareem, N. Morohashi, N. Nakagawa, J. Power Sources 172 (2007) 659–665.
- [15] J.G. Liu, T.S. Zhao, Z.X. Liang, R. Chen, J. Power Sources 153 (2006) 61–67.
- [16] Z. Guo, A. Faghri, J. Power Sources 167 (2007) 378–390.
- [17] Y. Yang, Y.C. Liang, J. Power Sources 165 (2007) 185–195.
- [18] <http://www.mtmicrofuelcells.com/technology>.
- [19] Q.-Z. Lai, G.-P. Yin, J. Zhang, Z.-B. Wang, K.-D. Cai, P. Liu, J. Power Sources 175 (2007) 458–463.
- [20] J. Liu, G. Sun, F. Zhao, G. Wang, G. Zhao, L. Chen, B. Yi, Q. Xin, J. Power Sources 133 (2004) 175–180.
- [21] R. Chen, T.S. Zhao, Electrochem. Commun. 9 (2007) 718–724.
- [22] M.S. Yazici, J. Power Sources 166 (2007) 137–142.
- [23] C. Arbizzani, M. Biso, E. Manferrari, M. Mastragostino, J. Power Sources 178 (2007) 584–590.
- [24] M.C. Lefebvre, Z. Qi, P.G. Pickup, J. Electrochem. Soc. 146 (1999) 2054–2058.
- [25] G. Wu, L. Li, J.-H. Li, Bo-Q. Xu, Carbon 43 (2005) 2579–2587.
- [26] C.T. Hable, M.S. Wrighton, Langmuir 9 (1993) 3284–3290.
- [27] A. Laborde, J.-M. Léger, C. Lamy, J. Appl. Electrochem. 24 (1994) 1019–1027.
- [28] J.-H. Choi, Y.-M. Kim, J.S. Lee, K.-Y. Cho, H.-Y. Jung, J.-K. Park, I.-S. Park, Y.E. Sung, Solid State Ionics 176 (2005) 3031–3034.
- [29] L. Niu, Q. Li, F. Wei, X. Chen, H. Wang, J. Electroanal. Chem. 544 (2003) 121–128.
- [30] J.-F. Drillet, R. Dittmeyer, K. Juttner, J. Appl. Electrochem. 37 (2007) 1219–1226.
- [31] G.H. Ayres, A.S. Meyer Jr., Anal. Chem. 23 (1951) 299–334.
- [32] T.C. Deivaraj, J.Y. Lee, J. Power Sources 142 (2005) 43–49.
- [33] J.H. Liu, M.K. Jeon, W.C. Choi, S.I. Woo, J. Power Sources 137 (2004) 222–227.