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Appropriate balance between methanol yield and power density in portable direct methanol fuel cell

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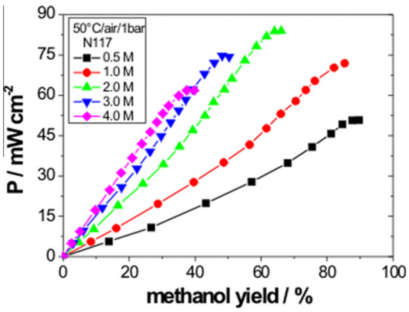
HIGHLIGHTS

- Optimization of DMFC performance with N117 at 50 °C for portable applications.
- Optimal balance between power density and methanol yield obtained with 1 M methanol.
- Methanol yield of 80% at low methanol concentrations and high current densities.
- Best performances with 2 mg cm^{-2} 50 wt% PtRu and cathode with microporous layer.

GRAPHICAL ABSTRACT



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ABSTRACT

This work aimed at the development of efficient catalysts and gas diffusion electrodes for a portable DMFC. The influence of catalyst loading, methanol concentration, working temperature, cell orientation, microporous layer and membrane thickness on 5 cm^2 cell performance were investigated. At 50 °C, a maximum power density of 84 mW cm^{-2} was calculated (50 mW cm^{-2} @ 400 mV) for the best performing MEA with a Nafion 117 membrane, 2 mg_{Pt} cm^{-2} at both anode and cathode with 2 M CH_3OH solution and air at ambient pressure. This good performance is attributed to both the highly dense and reactive catalysts as well as the presence of a microporous layer at the cathode that allows an optimal mass transport of reactants and products within the gas diffusion electrode. Methanol yield was found to be principally dependent on methanol concentration feed at the anode. Best performances in terms of methanol yield were obtained with the 0.5 M methanol solution and amounted to about 75% at 40 mW cm^{-2} @ 400 mV.

1. Introduction

The market for portable consumer electronics such as GPS, mobile phones or mp3 players is raising exponentially and as a consequence the demand for efficient, highly autonomic and low-cost portable power supplies, particularly for off-grid consumers. Since energy density of methanol (ca. 4.6 *vs.* 10 kWh kg^{-1} for gasoline and 33 kWh kg^{-1} for hydrogen [1]) is up to 50 times higher than that of a conventional rechargeable battery, the direct methanol fuel cell (DMFC) appears to be a promising power supply for these applications. Further advantages of methanol compared to hydrogen are simple handling, similar distribution and storage technology as used for gasoline. A survey of recent DMFC developments for portable applications is given in [2,3]. It should be noted that active systems generally exhibit higher output density (78 mW cm^{-2} @ 60 °C [4]) than passive ones (35 mW cm^{-2} @ RT [5]).

In 2009, the Toshiba Company has designed and commercialized a 5 W methanol-fuelled power supplier under the trade name

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Dynario™. Refuelling occurs by connecting a new methanol cartridge and takes only a few minutes. According to the supplier, however, the DMFC-based loading system must work in the vertical position. Until now, only a limited amount of 3000 units has been sold [6]. Some other similar DMFC-powered products such as Mobion (MTI) or SDI (Samsung) are more or less still in the prototype stage.

The development of a highly efficient orientation-independent DMFC is still a challenge. This is related to several system-inherent parameters such as slow reaction kinetics and high overvoltage of both the methanol oxidation reaction (MOR) and oxygen reduction reaction (ORR), creation of mixed potential at the air-cathode due to methanol permeation through the polymer electrolyte membrane, mass transport limitation of reaction products as well as poor corrosion resistance of catalysts [7]. Best performing benchmark catalysts up to now are PtRu and Pt for the anode and cathode, respectively. In order to reach an acceptable power density in the range of 100–200 mW cm^{-2}, high Pt catalyst loadings of about 1–4 mg_{Pt} cm^{-2} are commonly needed for both electrodes [8,9]. Also the long-term stability of the PtRu catalyst is still a crucial issue. Dixon et al. [10] claimed that the reduction of the PtRu oxide phase can create unalloyed Ru, that is assumed to be more susceptible to dissolution and cross over to the cathode side compared to the Ru alloyed with Pt. Precipitation of Ru on Pt active sites at the cathode lead to both significant decrease and increase of its activity for ORR and cathodic MOR, respectively. Park et al. [11] observed crossover of both Ru and Pt from the anode to the cathode due to decomposition of active Pt–Ru anode catalysts. The performance drop of the cell was explained by Pt contamination with Ru (max. 0.3 atom%) but also by the formation of Pt intermixture of defective nanocrystalline and amorphous structures at the cathode. The Ru crossover lowers the cell performance by up to 200 mV [12].

The reaction kinetics and methanol permeation through the polymer membrane are temperature-dependent. For non-pressurized systems, the temperature level is usually limited to about 80 °C at ambient pressure, which corresponds to maximal ionic transport of the perfluorinated Nafion 117 membrane. Methanol permeation through a Nafion membrane is driven principally by methanol diffusion and electro-osmotic drag [13]. At temperatures lower than 90 °C, Ren et al. [14] found that methanol concentration within the membrane pores is identical to that of the feed solution. However, at temperatures above 90 °C, the methanol concentration in the membrane pores decreased leading to a non-linear dependency of methanol flux with temperature, although the methanol diffusion coefficient increases with temperature. In the same work, the influence of membrane thickness on methanol diffusion was studied by operating the cell in electrolysis mode. At 70 °C, limiting current density values of 117, 132 and 335 mA cm^{-2} were measured for methanol oxidation in MEA with Nafion 117, Nafion 115 & Nafion 112 membrane, respectively. At 130 °C, j_{lim} reaches 425 mA cm^{-2} for the cell with Nafion 112 and about 195 mA cm^{-2} for both Nafion 115 and Nafion 117 equipped cells. Casalegno et al. demonstrate that, especially at open circuit voltage (OCV) while no methanol is consumed at the anode, methanol crossover rate culminates at values close to 2.5 mol s^{-1} cm^{-2} [15].

DMFC model analysis showed that methanol diffusion and electro-osmotic drag increase linearly with methanol feed concentration, whereas electro-osmotic drag contribution represents half of total diffusion at 0.3 A cm^{-2} current density [16]. The methanol yield is also strongly influenced by cell temperature and applied current density. At low current densities, methanol waste is much higher than anodic fuel utilization [17]. With increasing current density, however, crossover flow rate of a 1 M methanol solution decreased approximately linearly down to negligible values [18]. In order to reduce methanol crossover, several more or less efficient strategies such as Nafion-modified membranes, co-polymer, blend and composite membranes have been developed [19,20]. An overview of the most promising systems in terms of ionic conductivity and methanol selectivity is given by Deluca et al. [21] and Lufrano et al. [22]. However, the long-term stability of these membranes is still a crucial issue.

One established method for evaluation of the methanol crossover under fuel cell conditions consists in measuring CO_2 concentration in the cathode exhaust feed assuming that CO_2 permeation rate from the anodic chamber through the Nafion 117 membrane is negligible [23,24].

Mass transport of the reaction products carbon dioxide at the anode and water at the cathode is a limiting factor, especially at high current densities. It is meanwhile well known, that the presence of a microporous layer (MPL) positively influences distribution of reactants and water management at the cathode and may prevent cathodic flooding at high current densities [25,26]. By using a transparent cell, Spernjak et al. [27] observed water droplet formation at the anode and claimed that MPL creates a capillary-induced pressure barrier for water produced at the catalyst layer that is forced to back diffuse through the membrane and exit the anode flow field. The intercalation of a microporous layer (MPL) at the anode can also act as a methanol diffusion barrier and reduce methanol-crossover by up to 45% at low current densities [24]. Atiyeh et al. investigated the overall water balance in a H_2-PEM and found that the MPL neither affects the net drag coefficient nor supports water back diffusion from the anode to the cathode [28]. Results from an unstructured, two-dimensional pore network model of six commercial GDLs using an invasion percolation algorithm suggest that liquid water tends to accumulate in regions of high porosity due to associated lower capillary pressures [29]. A heterogeneous porous system seems to be the most appropriated structure for simultaneous water and gas transport in MPL/GDL [30]. High resolution X-ray radiographic imaging of an operating fuel cell reveals that liquid water was transported from the reaction layer to the GDL through the cracks in the MPL [31].

Efficient removal of CO_2 at the anode is also a key issue, especially in the case of passive or semi-passive DMFC systems where no active transport/convection of methanol exists, high methanol transport resistance in GDL is required to reduce methanol crossover and orientation of the cell differs [32–34]. Yang et al. [35] have examined CO_2 bubble behavior as a function of cell orientation by using transparent endplates. At high current densities, the difference in maximum power densities between vertical and horizontal alignment was about 10%. This was attributed to the fact that in vertical position, buoyancy force assists the removal of CO_2 gas bubbles on the top of the forced circulation of methanol solution that tends to suppress the formation of long gas slugs. At a current density of 150 mA cm^{-2}, the CO_2 bubble velocity in the exit region was about 55.7 mm s^{-1} for vertical and 50.0 mm s^{-1} for horizontal orientation. At low current densities, no significant change in cell performance was observed. Furthermore, a non-appropriated balance between hydrophobic/hydrophilic material properties of e.g. the flow field channel can lead to significant fluctuations in DMFC performance as well [36]. According to Burgmann's work, however, CO_2 bubbles may in some cases enhance methanol transport towards active catalyst sites and as a consequence stimulate the reaction rate [37].

This work aims at the optimization of parameters such as catalyst loading, methanol concentration and cell temperature for the development of an actively pumped orientation-independent 5 W (10 cell) portable micro-direct methanol fuel cell stack in connection with a micro structured methanol/water-mixer and membrane separator for CO_2 removal and a Li-ion battery as dynamic power supply.