

Distinct performance evaluation of a direct methanol SPE fuel cell. A new method using a dynamic hydrogen reference electrode

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Abstract

A stable reference electrode to be operated in a proton-exchange membrane direct methanol fuel cell (PEMDMFC) was strongly desired but is still lacking. Conventional reference electrodes known from aqueous systems are difficult to mount and to connect to the membrane electrolyte, and they introduce Donnan potentials into the system. It is shown in this study that a dynamic hydrogen electrode roughly maintains the thermodynamic hydrogen potential when operated at low cathodic current density sufficient to uphold the saturation with hydrogen of the electrode. Such a polarised auxiliary electrode allows the determination of a single electrode potential versus current density curves directly in the fuel cell, even during operation of the DMFC. A distinct determination of single electrode performance and fuel crossover is now possible.

Keywords. Hydrogen reference electrode, Methanol fuel cells

1. Introduction

As early as in 1964, Giner [1] showed that a dynamic hydrogen electrode (DHE) can be applied as reference electrode in electrochemical laboratory cells. It is particularly easy to use, does not require a salt bridge and does not pollute the system with unwanted anions or cations. A simpler variation of this electrode, the reversible hydrogen electrode (RHE), has found tremendous application in electrochemical research. The RHE, however, suffers from the fact that its hydrogen coverage is not constant as a function of time, and it is particularly sensitive to the adsorption of poisoning media such as simple organic molecules. The DHE does not show this disadvantage because its electrode coverage with hydrogen is forced to remain intact and hydrogen is in fact always supplied because a small cathodic current is continuously flowing through the reference electrode. In this way, the DHE may be called a stabilized RHE.

Therefore, the DHE should be an excellent candidate for a fuel cell reference electrode. Especially in cells using a solid polymer electrolyte, its use should be advantageous because the DHE can be directly mounted

very closely to the working electrodes of the fuel cell without using a salt bridge or any other electrolyte source. This avoids the introduction of corrosive species and membrane potentials into the system. The DHE has already been used in solid polymer electrolyte systems [2], but has never been applied to an operating fuel cell.

By utilizing a palladium-containing alloy, a remarkable stability of the reference potential can be attained through hydrogen storage in this material. Proper choice of auxiliary electrode materials appeared to be very important for stable operation. The potential was not affected by large amounts of gaseous methanol, and could be used as a stable reference in the presence of any otherwise electrode-poisoning fuel.

2. Experimental

Nafion™ 117 (Du Pont) was used in this experiment. Electrodes have been made from catalysed carbons (Heraeus and own manufacture) and carbon cloth 'GC-14' (The Electrosynthesis Co., USA) or purchased from E-TEK. Two 11 mm diameter platinised palladium-gold grids were used as DHE/auxiliary electrode

couple. The DHE current was usually supplied by a Hewlett–Packard 722 AR laboratory power supply; a galvanostatic circuit can be used for very precise measurements.

A schematic sideview of the cell bearing connected auxiliary electrodes has been given in Fig. 1. The auxiliary electrode shown at the left-hand (anode) side is used as DHE. It is mechanically pressed on to the membrane electrolyte. Application of a RHE connected to the cell via a tubing filled with liquid electrolyte (e.g., aqueous sulfuric acid) is also possible and has been used for the evaluation of DHE function.

Electrode membrane assemblies (EMAs) have been always manufactured using a hot-pressed procedure. After several variations, 50 bar and 130 °C were found to be suitable manufacturing conditions. This temperature just exceeds the glass transition temperature of Nafion (about 120 °C) and ensures that the membrane is soft enough to establish good contact with the electrocatalyst. The pressure is limited by the mechanical properties of the carbon cloth. We did not use pressures higher than 100 bar and did not observe any effect of pressure variation on electrode performance. The carbon cloth used as current collector was always GC-14

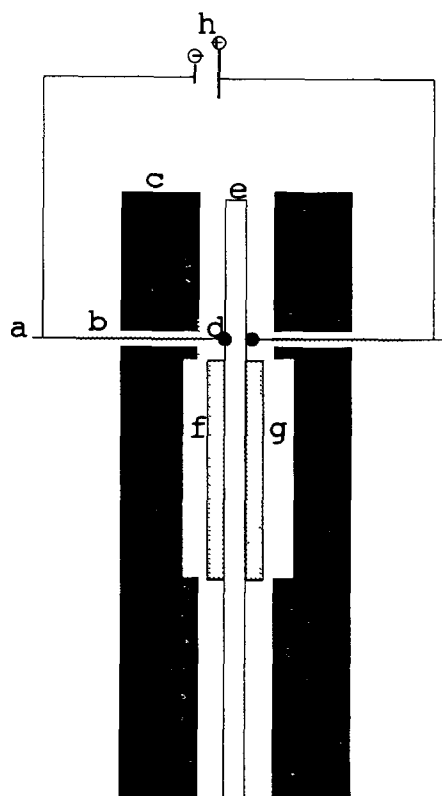


Fig. 1. Schematic view of the significant parts of the PEM fuel cell modified with auxiliary electrodes: (a) gold wire contacts; (b) PTFE insulators, (c) graphite gas manifolds and current collectors, (d) reference electrode (DHE), (e) proton-exchange membrane, (f) fuel cell anode, (g) fuel cell cathode, and (h) power supply for reference electrode.

from Electrosynthesis Co., USA. The catalyst was applied by mixing wet catalysed carbon with the desired amounts of alcoholic Nafion solution (perfluorosulfonic acid products) and polytetrafluoroethylene (PTFE) suspension (Hostafion, Hoechst, 60% in water) and spreading the resulting catalyst paste on to the as-received carbon cloth. This was followed by drying the electrode at 120 °C for 30 min. Finally, a second part of the Nafion solution was brushed on to the dry electrode in order to intensify the utilization of the catalyst on the surface area. This was followed by a repeated drying step. The resulting electrode of 5 cm² geometric area was not further treated but directly hot-pressed on to the ion-exchange membrane.

The EMA was mounted into the cell directly after hot-pressing manufacturing of EMA. The cell was equipped with the above-described auxiliary electrodes which were then pressed on to the membrane electrolyte when mounting the cell's end plates. The cell is in-house manufactured based on a commercially available model (Globe Tech). The application of the torque during the final cell mounting of the cell is a crucial factor for both the DHE function and EMA performance.

The palladium grid of the DHE was always precharged with hydrogen before fuel cell operation. A current of 3 to 10 mA at a cell voltage being just above 4 V was found to be suitable for this purpose. Both the membrane and the auxiliary electrodes were treated with distilled water before mounting the cell in order to enhance contact. After charging with DHE for about 15 min, the charging current was adjusted to 0.01 to 0.04 mA and held constant. By using hydrogen as anode feed and measuring open-circuit potentials, it was observed that the DHE potential amounted -20 to -40 mV versus RHE under these conditions.

A serious drifting behaviour of the DHE amounting ± 50 mV was observed after fuel-cell operation with hydrogen and oxygen at current densities up to 500 mA cm⁻². This is due to current density-dependent electroosmotic drag of water and proton transport across the membrane and, therefore, extreme changes in proton activity in the vicinity of the reference electrode. These main reasons of the drifting behaviour of the DHE reference electrode cannot be avoided. They also occurred during tests using a salt bridge connected RHE. The relation between potential deviation and operating current density will be a suitable objective for further research. However, reference drifting is much lower during DMFC operation because current densities exceeding 150 mA cm⁻² are rarely employed. Therefore, the DHE is especially useful in its purpose of DMFC performance monitoring. Much simpler RHE-like electrodes can be used for performance evaluation of hydrogen/oxygen PEMFCs [3].

The cell was heated to the operating temperature during 30 min and the EMA was allowed to equilibrate with water vapour and fuel gas at this temperature. Operating temperatures were 50 °C for operation with hydrogen and oxygen and 70 °C for DMFC operation. Water or methanol/water vapour were supplied by a gas-humidifying unit purchased from Giner, Waltham, MA, USA. Argon of high purity (Messer, Griesheim) was used as carrier gas for methanol/water vapour. Pure hydrogen (Messer-Griesheim) and oxygen were also used. Voltage versus current density measurements were performed directly after DHE charging and cell equilibration using an in-house built power supply at constant current drain. Data shown in the following Figs. are direct meter readings (METEX) determined after waiting for a constant reading.

3. Results and discussion

The DHE was first tested using hydrogen as anode feed. It was observed that the PTFE content of the electrode is of major importance, as illustrated in Fig. 2. Single electrode curves were measured during full cell operation. Negative shifts of working electrode potentials at open circuit or low current densities are due to the polarisation of the DHE, but the curves show significantly different slopes indicating that a PTFE content of 30 μl of PTFE suspension per 50 mg of catalyst powder (33% PTFE) are the closest approach to the optimum content. Further studies revealed the superiority of this amount. These preliminary results were used to design a Pt-Ru anode to be used in a DMFC. Its performance, as measured, using the DHE is shown in Fig. 3. It is clearly shown that a good hydrogen oxidation performance corresponds to good properties during methanol vapour oxidation, because it is obvious that the methanol oxidation potential ranges below 400 mV versus DHE when the cell is operated

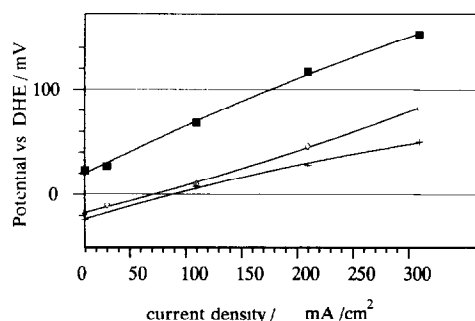


Fig. 2 Anode potential vs. current density for different hydrogen electrodes as part of EMA. Measurements were performed in the membrane fuel cell operated with hydrogen and oxygen at atmospheric pressure and 50 °C. Electrodes containing (■) 61%; (◇) 50% or (+) 33% PTFE in the electrode structure, respectively. Platinum loading: 1.6 mg cm⁻²

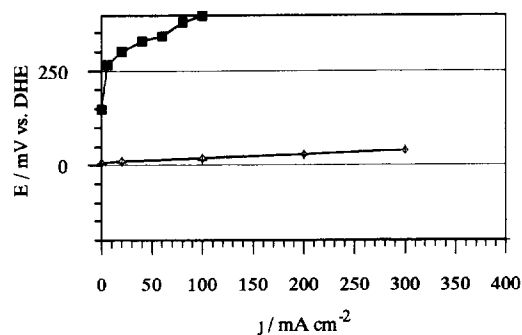


Fig. 3. Anode potential vs. current density for a Pt-Ru gas diffusion anode operated with methanol and hydrogen at different temperatures: (■) methanol at 70 °C; (◇) hydrogen at 80 °C, and (+) hydrogen at 50 °C. Noble metal loading of 2.5 mg cm⁻² on Norit BRX

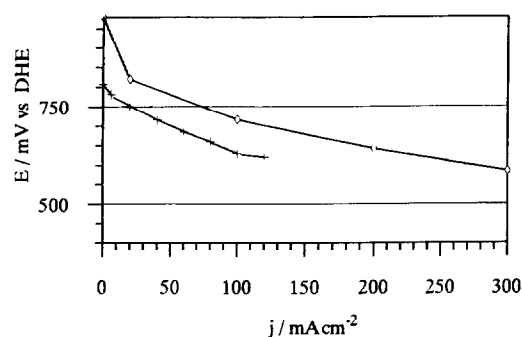


Fig. 4. Electrode potential vs. current density of an EMA oxygen electrode showing the effect of anode feed on oxygen electrode depolarisation. Measurements were performed in the membrane fuel cell operated with (◇) H₂/O₂ at 50 °C or (+) gaseous methanol/O₂ at 65 °C

at 100 mA cm⁻². Operation of the hydrogen fuel cell at 60 or 80 °C, respectively, does not show to have a significant influence on the performance of the hydrogen electrode.

It is of major importance, however, that the influence of methanol on the oxygen electrode characteristics can be clearly observed from single electrode curves. It is shown in Fig. 4 that the oxygen electrode experiences a shift of at least 100 mV when operated in a gas-fed DMFC. This effect is due to the methanol crossover across the NafionTM membrane. It is therefore evident that the design of a reference electrode was needed to find out where to locate the losses of the DMFC.

4. Conclusions

A reliable DHE reference electrode was introduced into a proton-exchange membrane direct methanol fuel cell (PEMDFC), and was used for a distinct single electrode characterisation. Our results enabled us to

conclude that the electrocatalysis of methanol oxidation has reached the stage where satisfying anode performances can be obtained. Our anode performance is acceptable when the relatively low noble metal loading of 2.5 mg cm^{-2} has been applied. Significant losses of cell voltage can be attributed to slow cathodic oxygen reduction kinetics in general and to methanol crossover in the DMFC. Improvements should be made in the fields of membrane design and cathode optimisation rather than in the design of the anode.

Acknowledgement

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