Methanol permeability in perfluorosulfonate proton exchange membranes at elevated temperatures

P. S. KAURANEN*, E. SKOU
Odense University, Department of Chemistry, Campusvej 55, DK-5230 Odense M, Denmark

Received 25 September 1995; revised 11 December 1995

A simple electrochemical method for the measurement of the permeability of methanol in proton exchange membranes equilibrated with a supporting liquid electrolyte at elevated temperatures is proposed. Carbon supported platinum working electrodes are placed to both sides of the membrane sample and serve as concentration sensors. Methanol is added to one or both sides of the membrane and the permeability is calculated from the time responses of anodic peak currents on the two working electrodes. Experimental results are given for Nation® 117 perfluorosulfonate membrane in 2.0 M H₂SO₄ at 60 and 70 °C.

1. Introduction

There has been renewed interest in the direct oxidation methanol fuel cell (DMFC) concept during the last few years. This has mainly been due to the improvements of the methanol oxidation catalyst performance based on improved fundamental understanding of the basic reaction phenomena on platinum based alloys [1-3]. Furthermore, the use of perfluorosulfonate proton exchange membranes, e.g. Nafion® 117 by DuPont, has made it possible to increase the reaction temperature to 80–110 °C which has lead to considerable improvements as compared to earlier work in sulfuric acid at 60 °C [4–6]. However, perfluorosulfonate membranes are known to be quite permeable to methanol [7, 8] leading to methanol crossover to the oxygen cathode in the DMFC. This crossover causes losses in terms of lost fuel and cathode depolarization due to a mixed oxygen reduction/methanol oxidation potential at the cathode [9–12]. Despite these setbacks the perfluorosulfonate membranes have been successfully applied to DMFC single cells [5, 6].

Methanol can be supplied to the DMFC anode as a dilute solution in water either in liquid or vapour phase [5, 6]. The liquid feed concept would be highly preferred from an engineering point of view due to a more compact design and simplified thermal and water management in the DMFC stack [5].

Verbrugge [7] has used a radioactive tracer method to measure the methanol diffusivity in Nafion® equilibrated with sulfuric acid at room temperature. The method appears very accurate and may be used for further analysis, but special equipment and radio isotopes are needed to carry out such experiments. Furthermore, Kato et al. [13] has reported on permeabilities of different alcohols in Nafion®. However, as they used trimethyl ammonium (CH₃)₃NH⁺ as the counter ion and the other membrane surface

* Permanent address: Helsinki University of Technology, Department of Technical Physics, FIN-02150 Espoo, Finland

List of symbols

\[A \quad \text{geometric area (cm}^2\text{)}\]
\[c \quad \text{concentration (mol cm}^{-3}\text{)}\]
\[D \quad \text{diffusivity (cm}^2\text{s}^{-1}\text{)}\]
\[E \quad \text{potential vs RHE (V)}\]
\[\Delta E \quad \text{activation energy (kJ mol}^{-1}\text{)}\]
\[H \quad \text{Henry law constant (atm mol}^{-1}\text{cm}^3\text{)}\]
\[j \quad \text{current (mA)}\]
\[K \quad \text{rate constant (cm}^3\text{s}^{-1}\text{)}\]
\[K^* \quad \text{partition coefficient}\]
\[l \quad \text{thickness (cm)}\]
\[N \quad \text{molecular flux (mol cm}^{-2}\text{s}^{-1}\text{)}\]
\[p \quad \text{pressure (atm)}\]
\[t \quad \text{time, (s)}\]
\[T \quad \text{temperature (°C)}\]

\(V \quad \text{volume (cm}^3\text{)}\)
\(\varepsilon \quad \text{volume fraction}\)
\(\tau \quad \text{time constant (s)}\)

Superscripts and subscripts

d \quad \text{diffusion}
e \quad \text{evaporation}
i \quad \text{index, 1: glass cell; 2: sample holder}
max \quad \text{maximum}
Me \quad \text{methanol}
ref \quad \text{reference}
w \quad \text{water}
t \quad \text{total}
0 \quad \text{initial double layer charging}
l \quad \text{anodic peak}
was facing a vacuum in their experiments, their work has little relevance to DMFC application. Thus, the permeability of methanol in perfluorosulfonate membranes at practical DMFC operation temperatures is still not well known, leading to some uncertainty of the extent of the crossover flux and its importance to the overall cell energy balance and efficiency [8, 9]. Furthermore, simple methods based on generally available equipment to measure the permeability would be of considerable value in comparing different pretreatment methods for perfluorosulfonate membranes or alternative electrolyte membranes [14] with the presently used materials.

In this paper we present a simple electrochemical method to measure methanol permeability in proton exchange membranes. The method is applied to measure methanol permeability in Nafton® 117 in the temperature range 60–70 °C. The problems associated with the present setup are discussed and an improved setup proposed.

2. Experimental details

The membrane sample was placed into a PTFE sample holder on top of a thermostated Pyrex glass cell with a 2.0 M sulfuric acid supporting electrolyte, see Fig. 1. The liquid volumes were 20 ml in the sample holder and 125 ml in the glass cell. One platinum working electrode serving as a methanol concentration sensor was placed in the sample holder and another in the glass cell. A mercury/mercurous sulfate (MMS) reference electrode and a platinized platinum foil counter electrode were placed in the glass cell. Both volumes of the supporting electrolyte were agitated by magnetic stirrers and purged continuously with nitrogen. The potentials of the working electrodes were controlled by means of a potentiostat, and a switching relay with a timer was used to switch between the two working electrodes.

Methanol was added to one or both sides of the membrane and the time response of the working electrodes were recorded in a 30 min switch on/switch off sequence. During the switch on sequence the working electrode was continuously cycled at 25 mV s⁻¹ between predetermined potential limits in the double layer region of the platinum surface [3, 15] and the peak current in the anodic scan of the voltammogram was taken as a measure of methanol concentration. The potential limits were selected to avoid any contribution of hydrogen desorption or oxygen adsorption to the anodic peak current and in a way that the methanol oxidation peak lay well within the scanning region over the whole concentration range of interest, see Table 1. The scanning rate was selected as a compromise between minimum double layer charging current at zero methanol concentration and maximum number of cycles during the switch on sequence. Finally, the peak currents over the 30 min switching sequence were averaged for further analysis.

Rather low methanol concentrations were used to ensure linear concentration current response, and to minimize the ohmic losses as well as convective methanol transport in electroosmotic water flow [16, 17] through the membrane. For the same reasons, relatively small working electrodes of 4.0 mm in diameter were used. 40 wt % Pt on carbon (XC-72R by E-TEK Inc.) was used as the catalyst material on the working electrodes. PTFE bonded and carbon cloth supported electrodes were fabricated according to [18].

The vertical setup was problematic because some air became trapped below the membrane sample when the sample holder was placed on the top of the glass cell. Very extensive stirring was needed in the glass cell to remove this trapped air and further to prevent the accumulation of CO₂ or H₂ produced at the working and counter electrodes, respectively, under the sample holder during the experiment. The extensive stirring, in turn, caused dissolution of oxygen from the surrounding air to the supporting electrolyte which was clearly seen as asymmetry between the anodic and cathodic scans at zero methanol concentration. Continuous nitrogen bubbling was needed to suppress the oxygen dissolution to acceptable limits.

Nafton® 117 membrane was boiled in dilute H₂O₂, distilled water and 1.0 M sulfuric acid before the experiments [17], and equilibrated for a minimum of

| Table 1. Scanning limits for the voltammograms |
|---|---|---|
| T /°C | E_{low} /V vs RHE | E_{high} /V vs RHE |
| 60 | 0.30 | 0.80 |
| 70 | 0.25 | 0.75 |