Mass Transport in the Membrane of a DMFC

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Crossover of methanol in the direct methanol fuel cell (DMFC) is a serious problem when using currently available membrane electrolyte materials, *i.e.* Nafion. The methanol permeation significantly worsens fuel cell system performance. This is due mainly to the mixed potential that is the result of methanol being oxidised on the cathode, something that can severely lower the power output of the cell, but also to the lower overall fuel utilisation grade.

The purpose of this work is to develop a model that describes the mass transport of water and methanol, together with the conductive transport of protons, in the electrolyte, thereby enabling calculation of the effects of methanol permeation on fuel cell performance. Previous DMFC models have treated the membrane as a dilute solution where standard Fick's law diffusion have been assumed, in which case diffusion and electro-osmotic drag has to be treated separately [1,2]. Some hydrogen/oxygen PEFC models have used the Stefan-Maxwell equations to describe the mass transport model [3,4]. The Stefan-Maxwell electrolyte approach, working with binary diffusion coefficients, takes into consideration simultaneously the concentration and potential gradients as well as the electro-osmotic drag of solvent.

Fuel cell performance studies indicate however that the methanol feed concentration, and consequently the concentration in the membrane, can be significantly higher than would normally be considered a dilute solution, especially for vapour feed DMFC [5,6]. This would be of particular importance if one considers the possibility of developing methanol resistant cathode catalyst materials. Concentration dependence on diffusion coefficients has been reported for both water and methanol [3,7,8]. The diffusion coefficient of methanol measured in a Nafion membrane with low total solvent content exhibits strong concentration dependence. This could also be imagined to occur for higher total solvent content as methanol concentration increases, since methanol dissolves in the membrane structure. This methanol uptake alters the mechanical properties of the polymer, leading to increased mobility of the side chains and thereby possibly affecting the transport properties of the electrolyte membrane [8,9]. The electro-osmotic drag of water and methanol is also influenced by the solvent concentration.

The aim is therefore to investigate the effects of higher methanol concentration on the applicability of the dilute and concentrated electrolyte models. In achieving this for the direct methanol fuel cell, the Stefan-Maxwell mass transport equations of a four species concentrated electrolyte are solved for experimentally obtained mass transport data. Experiments are designed so as to enable determination of the six relevant binary diffusion coefficients, the parameters expressing the level of interaction between the different species present in the electrolyte, from the three independent transport equations. The concentration dependence of the binary diffusion coefficients is investigated and determined.

The extent of methanol crossover and water transport is measured in a fuel cell during operation, using a mass spectrometer to register methanol, water, and CO_2 in the exhaust gas. The measurements are carried out under realistic fuel cell operating conditions on a laboratory scale (1 cm^2) single cell DMFC. Nafion 117, a well-known and well-characterised material, is initially used as membrane material, in order to establish the experimental and computational methodology. Transport data is registered for a range of operating temperatures and methanol feed concentrations. The thus obtained transport data are used to solve the system of transport equations, and hence, in the calculation of the binary diffusion coefficients. The concentration dependence of the diffusion coefficients is investigated. Results are validated against transport data obtained through limiting current measurements. In future work, the same modelling approach and experimental measurement technique will also be applied to other types of perfluorosulfonic acid membrane materials.

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