Chemical Engineering Science 143 (2016) 181–193

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Model-based analysis of water management at anode of alkaline direct methanol fuel cells

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HIGHLIGHTS

- First modelling study of water management at anode of anion-exchange membrane ADMFCs.
- Effect of unstable water level in the anodic loop of an ADMFC is demonstrated.
- Conditions that lead to stable water level in the anodic loop are identified.
- Full humidification of inlet gases is detrimental for stable water level in AFCs.
- Importance of quantification of water diffusion for design of ADMFC-systems revealed.

ARTICLE INFO

Article history:
Received 25 August 2015
Received in revised form
7 December 2015
Accepted 11 December 2015
Available online 7 January 2016

Keywords:
ADMFC
Fuel cell system
Anion exchange membrane
Alkaline fuel cell
Water management
Mathematical modelling

ABSTRACT

Alkaline direct methanol fuel cells (ADMFCs) produce water at the aqueous fed anode. This complicates water management at anode which is analysed in this study by modelling three extreme case scenarios assuming different conditions for water transport or removal. All scenarios include recycling of methanol solution at anode outlet to achieve high methanol efficiencies. One scenario reveals that high operation times and high methanol efficiencies necessitate active stabilisation of anodic water level since both water accumulation and depletion can take place depending on operation conditions. Another scenario shows that water level can be stabilised by adjusting cathodic evaporation and the corresponding water removal from the system. The results indicate that feeding cathode with water-saturated gas is detrimental for stabilising water level. The last scenario suggests the addition of a gas flow to anodic outlet to remove excess water for water level stabilisation. Minimization of additional methanol loss requires to reach high humidities by evaporation. The present paper reveals the impact of processes occurring in ADMFCs on anodic water management and indicates the necessity to quantify water transport through membrane. Knowledge of the influence of operation conditions on water level in the anodic loop are beneficial for design of ADMFC systems.

1. Introduction

One of the main reasons why fuel cells are not commercialised yet is the high cost which mainly comes from expensive materials. A potential way of reducing the cost of fuel cells is to use fuel cells of the alkaline type which do not require platinum as catalyst. Due to higher activity and stability in alkaline media, even non-precious metals like nickel can be used as catalyst. However, alkaline fuel cells used to be operated with liquid electrolyte which causes, among others, corrosion and carbonation problems. The latter is quite intense in alkaline direct methanol fuel cells (ADMFCs) since CO_2, which causes the carbonation, is permanently produced at anode during operation. In order to avoid these problems, anion exchange membranes were introduced as electrolyte in alkaline fuel cells as reported by Varcoe et al. (2006). Thus, research of alkaline fuel cells mainly focusses on new catalysts (Varcoe et al., 2008; Yu et al., 2010) or new membrane material (Merle et al., 2011; Cheng et al., 2015). A very detailed overview over state of the art of anion exchange membranes (AEMs) and their application in electrochemistry is given by Antanassov et al. (2014) who also state that low conductivity and poor stability of AEMs are still challenging topics. Up to now alkaline anion exchange membrane fuel cells do not show the same performance as acidic fuel cells (Varcoe and Slade, 2006) or

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http://dx.doi.org/10.1016/j.ces.2015.12.006
0009-2509/

alkaline fuel cells with liquid electrolyte (Coutanceau et al., 2006; Janarthanan et al., 2015). The reason for that low performance is not clear yet since removing the alkaline solution effects several things such as ionic conductivity, reaction kinetics, and water management. Most studies about anion-exchange membrane fuel cells focus on performance of the fuel cells with new component materials (Janarthanan et al., 2015; Yu and Scott, 2004; Sun et al., 2012; Poynton et al., 2010). Modelling studies also describe and analyse mainly the performance of AFCs (Kimble and White, 1991; Jo et al., 2000; Mohan and Shrestha, 2010; Verhaert et al., 2009; Jiao et al., 2014; Verma and Basu, 2007; Deng et al., 2014; An et al., 2013) considering ion conduction and reaction kinetics while process engineering issues remain unstudied. Due to the low performance without liquid electrolyte, most studies about alkaline direct alcohol fuel cells include potassium or sodium salts mixed to alcohol solution for a better performance as summarized by Antanassov et al. (2014). Likewise, the few models of alkaline direct alcohol fuel cells mostly include KOH or NaOH solution in addition to the electrolyte membrane (Verma and Basu, 2007; Deng et al., 2014; An et al., 2013; Bahrami and Faghri, 2012). Only few exceptions consider solely an anion-exchange membrane as electrolyte in ADMFCs (Weinzierl and Krewer, 2014; Deng et al., 2015).

Although water transport through the membrane has already been identified as a possible limiting factor for performance of AFCs by Poynton et al. (2010), water management attracted little attention so far. Only in few studies, water transport coefficients through anion-exchange membranes have been determined experimentally (Li et al., 2010; Follain et al., 2012; Garca-Nieto and Barragn, 2015) or have been estimated by modelling (Myles et al., 2011; Yamanaka et al., 2009). Whereas water transport processes have been included in many mathematical models of AFCs (Kimble and White, 1991; Jiao et al., 2014; Deng et al., 2014; Weinzierl and Krewer, 2014; Deng et al., 2015; Bjornbom and Yang, 1993; Yang and Bjornbom, 1992; Huo et al., 2012; Deng et al., 2013), the effect of water management was only studied for AFCs with liquid electrolyte by Verhaert et al. (2011) and Rowshanzamir et al. (1998), for the anode of hydrogen fuelled AEMFCs by Huo et al. (2012) and Deng et al. (2013) and for an AEM ADMFC cathode by Weinzierl and Krewer (2014) so far.

Direct methanol fuel cells (DMFCs) are highly attractive for portable and off-grid applications due to the high energy density of methanol. To reduce the weight of DMFC-systems and to achieve high methanol efficiencies, recycling of methanol solution is applied. This causes a special need to maintain constant amount and composition of the liquid in the anode loop. Stable and autonomous operation of methanol fuel cell systems without refilling water or storing waste solution has already been analysed for acidic DMFC-systems by Zenith et al. (2010). In acidic DMFCs, water is lost at anode and needs to be recovered from the cathode exhaust whereas it is not clear yet whether water accumulation or depletion takes place in the anode compartment of an alkaline DMFC. Therefore, our previously published model (Weinzierl and Krewer, 2014) that was used to analyse water management at cathode is extended in the present paper in order to analyse water management at anode of an ADMFC. It targets to determine conditions that lead to stable water level and to reveal the effect of unstable water level on methanol efficiency and operation time. Furthermore, this study identifies the influence of conditions at cathode on the anodic water level as well as one way of removing water from anodic liquid and the consequences of that removal on efficiency.

2. ADMFC-system structure and relevance of water management

The anode of an ADMFC is fed with water-methanol-solution and the methanol is electrochemically oxidised as follows:

$$CH_3OH + 6OH^- \longrightarrow CO_2\uparrow + 5H_2O + 6e^- \quad (1)$$

while cathode reaction is:

$$\tfrac{3}{2}O_2 + 3H_2O + 6e^- \longrightarrow 6OH^- \quad (2)$$

This results in the following overall reaction:

$$CH_3OH + \tfrac{3}{2}O_2 \longrightarrow CO_2 + 2H_2O \quad (3)$$

Water is dragged along with the OH^--ions from cathode to anode. Due to the methanol-water solution that is fed to anode, a gradient between high concentrations at anode and low concentrations at the gas fed cathode is formed which leads to water diffusion as well as methanol diffusion through membrane from anode to cathode. The latter is called methanol cross-over. In order to avoid fuel starvation, methanol is fed in excess. To prevent waste of methanol it is necessary to recycle the liquid leaving the anode chamber. Methanol concentration is low (≈ 1 moll^{-1}) to avoid high methanol losses due to cross-over. Hence, most of the recycled liquid is water. Fig. 1 shows an ADMFC connected to an anodic loop to recycle methanol solution. The gas in the flow leaving the anode needs to be removed for example by a membrane separator

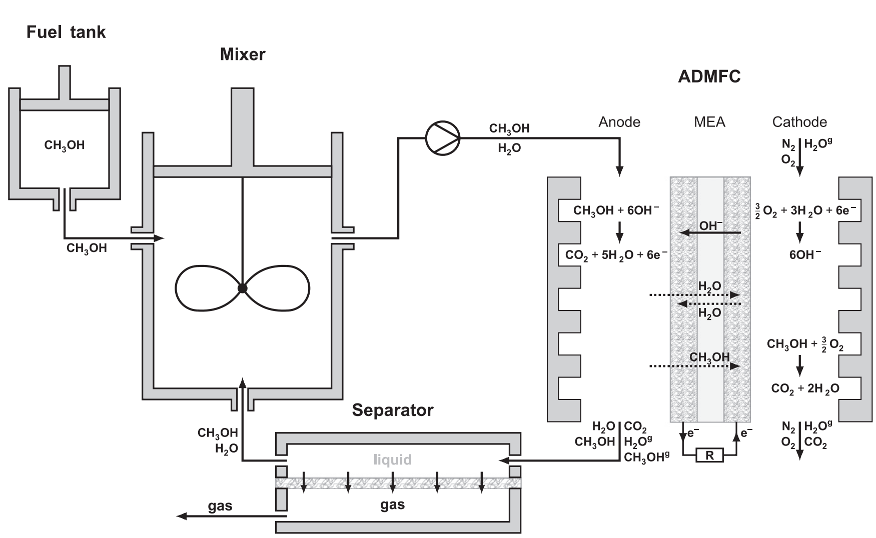

Fig. 1. Schematic of an ADMFC system including fuel tank, membrane separator, mixer and ADMFC with anode, cathode and membrane electrode assembly (MEA).