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Model-based analysis of anion-exchanger positioning in direct methanol fuel cell systems

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HIGHLIGHTS

- We studied the impact of carbon dioxide on the design of active portable DMFC systems with a model-based approach.
- It is discussed how the concentration of carbon species is effected by methanol concentration in methanol–water-solution.
- The amount of carbon species in dependency of the temperature and partial pressure is presented.
- Study of the position and design of the anion exchanger in the anode loop under the aspect of portability.
- Influence of the gas liquid separator design on carbon species concentration is presented.

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ABSTRACT

In this work we present a model based study to investigate the presence of anion exchangers in direct methanol fuel cell (DMFC) systems. It is well known that environmental or fuel impurities lead to accumulation of harmful anions, such as chloride, in the system. However, due to DMFC anodic reaction, a carbonate system is present. These corbanate anions have to be taken into account for the anion exchanger design and placement as well as for the system operation strategy with and without anion exchanger, which is the objective of this study. For this purpose, the expected amount of harmful chloride ions in a DMFC system is estimated, and that of carbonate ions is calculated with a model of the carbonate system in a DMFC system. The predicition of durability and dimensions of an anion exchanger is based on a monovalent anion exchange model. The design of gas liquid separators in the DMFC system has a major influence on the amount of dissolved carbon dioxide, which is crucial for durability and dimension of a system integrated anion exchanger. Finally, feasible positions of anion exchanger in a DMFC system are elaborated to fulfill the needs for long term and stable DMFC operation.

1. Introduction

Direct methanol fuel cell (DMFC) systems are attractive energy sources for portable appliances. In order to prevent DMFC degradation, the accumulation of ionic species in the DMFC system from various sources should be avoided, as they negatively affect DMFC system performance [1–4]. Specifically, Cl^- enters the system as an impurity in fuel cell components, such as catalyst layer or membrane, or as a pollutant in the charged air. Due to water recovery from the cathode side and the presence of NH_4Cl in the supplied air [3], an enrichment of Cl^- in the anode loop is possible. Besides, an enrichment of metal and non-metal ions in the anode solution and in the membrane electrode assembly (MEA) of the DMFC was found to cause significant performance issues [5].

To avoid the before mentioned accumulation of harmful ionic impurities in the anode loop, including anion exchangers into the DMFC system has been proposed [5]. However, the application of anion exchangers in DMFC systems is strongly influenced by the DMFC system itself. Due the production of CO_2 in the DMFC anode reaction, CO_2 dissolves and forms carbonate species such as hydrogen carbonate (or bicarbonate), HCO_3^-, and carbonate ions, CO_3^{2-} [6,7]. In a DMFC system with an anion exchanger in the anode loop, these anionic carbon species rival with anions from impurities

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for the ion exchange and can therefore determine the durability and dimension of the applied anion exchanger.

In this paper, we evaluate the feasibility of an anion exchanger and its placement in a DMFC system. First we estimate the amount of harmful ions like Cl^- as well as the amount of carbonate species which occur at different positions in the DMFC system. This is done by means of a systematic investigation of the present carbonate system in the DMFC system. A model based approach is applied to account for the amount of dissolved carbonate species as a function of operating parameters of the fuel cell, such as temperature and methanol concentration. Secondly, a monovalent anion exchanger model is set up and charged with different flow rates of solution containing varying concentrations of before mentioned anions to determine its durability and dimensions. As a result, we show that, depending on the gas phase above the solution, carbonate systems occur in the DMFC system: the semi-open carbonate system is expected in the gas liquid separator, whereas the closed carbonate system exists in the DMFC anode compartment and all other parts of the anode loop, especially in the anion exchanger. The occurrence of different carbonate systems influences the position of the anion exchanger. Based on these results, we demonstrate which anion exchanger positions in the DMFC system are feasible to fulfill the needs for long term and stable operation.

2. Methods and preliminary considerations

In the following section, the expected amount of ion species of chloride and carbonate ions is estimated and the essential model equations for this work are derived. The DMFC system considered in this work is sketched in Fig. 1. It consists of the DMFC, the gas liquid separator at the anode side, the liquid gas separator at the cathode side, the methanol supply with methanol tank and fuel pump, and the respectively placed anion exchanger in the anode loop.

Expected amount of chloride impurities. Chloride ion impurities can enter the DMFC anodic loop via the neat methanol solution used, which possesses a given chloride impurity of 0.5 ppm that results in 1×10^{-5} mol l^{-1} Cl^- for 1 M methanol solution. Another source of chloride ions is the liquid gas separator behind the DMFC cathode compartment where product water is recycled and fed back to the anodic loop. Due to the usage of atmospheric oxygen the concentration of methyl chloride (CH_3Cl), which is the most abundant halocarbon in the atmosphere and therefore the most important source for chloride anions, reaches average values of approximately 500 ppt [3]. Due to the very low solubility of chloride in water [8], we estimate a concentration of 2×10^{-7} mol l^{-1} dissolved Cl^- for this work.

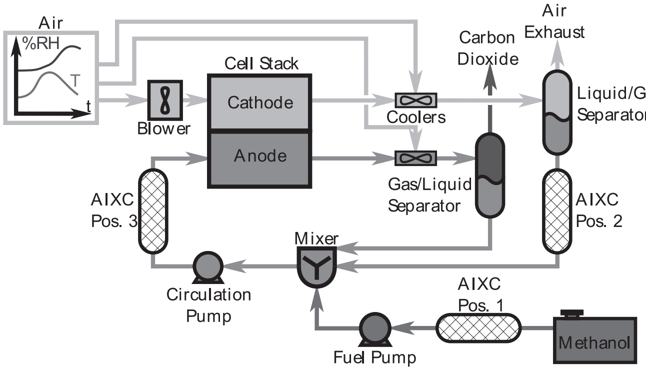

Fig. 1. Schematic of the DMFC system with different options for positioning the anion exchanger. The DMFC system is described in more detail elsewhere [23].

2.1. Expected amount of carbonate ion species

If gaseous CO_2 is in contact with an aqueous solution, it partly dissolves in the solution and a carbonate system evolves. In the following, we give a brief introduction on the carbonate system and investigate its appearance in DMFC systems.

Dissolved CO_2 yields three different inorganic species in aqueous solutions: dissolved carbon dioxide, CO_2(diss); bicarbonate, HCO_3^-; and carbonate ion, CO_3^{2-}. All together constitute the carbonate system [6] and their individual concentrations are related as follows:

$$[CO_2(\mathrm{diss})] \equiv H^*_{CO_2} \cdot p'_{CO_2} \tag{1}$$

$$\left[H^+\right] \cdot \left[HCO_3^-\right] = [CO_2(\mathrm{diss})] \cdot K_{a1} \tag{2}$$

$$\left[H^+\right] \cdot \left[CO_3^{2-}\right] = \left[HCO_3^-\right] \cdot K_{a2} \tag{3}$$

$$\left[H^+\right] \cdot \left[OH^-\right] = K_W \tag{4}$$

where concentrations in liquid phase are indicated with square brackets and the unit of $H^*_{CO_2}$, Henry's law coefficient, is mol l^{-1} [9]. K values indicate the pressure and temperature dependent dissociation constants. K_W is referred to as the ion product of water. The respective constants used in the present work are given in Table 1.

Consequently, the carbonate system is described completely with the use of Equations (1)–(4), the sum of all dissolved carbon dioxide species (DIC) (5) and the electroneutrality condition (6):

$$\mathrm{DIC} = \left[HCO_3^-\right] + \left[CO_3^{2-}\right] + [CO_2(\mathrm{diss})] \tag{5}$$

$$0 = \left[H^+\right] - \left[HCO_3^-\right] - 2 \cdot \left[CO_3^{2-}\right] - \left[OH^-\right] \tag{6}$$

The influence of methanol on the dissolution of carbon dioxide is given by Ref. [13]. Since, a highly diluted methanol water solution is expected at the anode outlet, the influence of methanol on the carbonate system can be neglected for DMFC operation. This accompanied by considering the methanol influence on Henry's law coefficient for the carbonate system as described in Section 2.2.

Depending on the properties or existence of a gas phase above a solution, the carbonate system can be classified as open (a), closed (b) or semi-open (c) carbonate system [6]. The open system is the most complex, as found e.g. in sea water systems in contact with environmental air. We consider it as not relevant for DMFC operation. The semi-open system possesses a gas phase with a constant amount of gaseous carbon dioxide with a constant partial pressure p'_{CO_2} as it may occur in certain parts of the DMFC system. The closed system possesses no gas phase above the solution that interacts with the environmental atmosphere. A schematic representation of the carbonate systems used in this work, is depicted in Fig. 2. In the same figure, an overview on the expected amounts of carbonate species is given for the closed carbonate system and the semi-open carbonate system. The minimal depicted partial pressure is set to the expected partial pressure of carbon dioxide in the atmosphere of about 3.535×10^{-5} MPa, whereas the maximal depicted partial pressure is equal to atmospheric pressure of 0.101325 MPa at 298 K. According to $p'_{CO_2} = 0.101325$ MPa given by the anode side gas liquid separator, the aqueous methanol solution will be present with a maximal possible concentration of dissolved carbonate of $c_{CO_2(\mathrm{diss})} = 2.26 \times 10^{-2}$ mol l^{-1}. Table 2 lists all relevant DMFC