Extending the lifetime of direct methanol fuel cell systems to more than 20,000 h by applying ion exchange resins

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A B S T R A C T

Over the last few years, we have developed a 1.3 kW direct methanol fuel cell (DMFC) system with a proven lifetime of 20,000 h. An extension of the system's lifetime would dramatically increase the commercial competitiveness of this technology. In order to reduce degradation effects in the stack, we identify the insertion of ion exchange filters into the anodic circuit as an important approach for absorbing impurities directly in the fluid cycle. This paper outlines the development of a characterization technique and material screening process for ion exchange materials, which are characterized in terms of their stability, activity and capacity, as well as their selectivity under the operating conditions of a DMFC system. The amount of ion-exchanging material is calculated by means of a project post-mortem analysis of a DMFC stack operated for 20,000 h. This study fills a gap in the literature and offers a basis for the designing of ion exchangers. The results presented are an important step for the ongoing development process and commercial deployment of DMFC systems. Given the similarity of requirements, the results are also applicable to the PEM electrolysis field.

Introduction

Fuel cells are electrochemical energy converters that can generate electrical energy from fuel. Since a thermal process is not necessary for this conversion, high degrees of efficiency are feasible even for compact, portable fuel cell systems [1].

In many available fuel cell systems, hydrogen is used as an energy carrier. But for power ratings below 5 kW, methanol is a promising alternative to hydrogen in this capacity [2,3]. On

the one hand, methanol is easy to handle due to its liquid state and has an energy density some four times higher than pressurized or liquefied hydrogen. On the other, methanol can be utilized directly as a fuel in *direct methanol fuel cells* (DMFCs), thus simple fuel cell systems can be realized without extensive conversion processes to generate fuel gas [4].

Over the last decade, the IEK-3 at the Forschungszentrum Jülich has developed DMFC systems for different applications. One successful development was that of a 1.3 kW DMFC system for a horizontal order picker. Most recently, a 4 kW DMFC

system has been developed as an *uninterruptible power supply* (UPS) that can be applied to mobile radio applications, for instance. This DMFC system has a proven lifetime of more than 20,000 h [5]. However, to compete with conventional technologies on the UPS market, it will be necessary to reach a lifetime of ten years (discontinuous operation) [2].

To extend the lifetime of fuel cell stacks and therefore the MEAs assembled, the degradation mechanisms of *membrane electrode assemblies* (MEAs) must be examined, evaluated and inhibited as far as possible. A variety of degradation effects can be identified in the literature and these contain different chemico-physical mechanisms responsible for performance losses. These losses can be distinguished by reversible and irreversible degradation [6–10]. Reversible performance losses are defined as losses that can be compensated by changing the electric load or air flow of the fuel cell stack [11–13]. Mechanisms responsible for reversible degradation of DMFC MEAs include the oxidation of platinum catalysts at the cathode, temporary membrane dehydration and incipient cathode flooding [14–16]. Furthermore the performance of a cell may be affected by insufficient transport of produced water respectively produced CO_2 out of the cell [17]. Aging and re-aging due to reversible effects take place within minutes or hours, but due to its reversibility it does not have to be considered to improve the long-term stability of MEAs.

To achieve a service lifetime of more than 20,000 h with DMFC systems, it is necessary to inhibit the irreversible degradation effects they are prone to. The mechanisms responsible for permanent performance losses of MEAs are explained in numerous articles [14–16,18]. Summarized irreversible aging processes lead to a reduction of the electrochemically active area of MEAs. The reasons for this include reduction of the catalyst's activity due to poisoning, ruthenium crossover or the growth of the catalyst's particle size (loss of active surface). A further reason for irreversible aging processes can be given by an improper supply with reagents due to the loss of hydrophobicity on the cathode side. Important studies deal with methods to predict the degradation of DMFC cells [19,20].

A very strong negative effect on the long term stability of the MEA is caused by contamination with organic or inorganic materials [21,22]. Possible sources of organic contamination are unsuitable polymers or elastomers, as well as sealings, adhesives or lubricants used in the stack or the peripheral components of the DMFC system. These materials may emit contaminations, especially if they come into contact with the methanol–water solution of the anodic cycle. Many organic contaminations are suspected of poisoning the catalyst. Similarly harmful is contamination with inorganic materials. Possible sources of this include metal parts (tubes, condenser, and metallic bipolar plates) in the fuel cell system that may be affected by corrosion. Other types of inorganic or organic contaminants may also enter the system via contaminated fuel [23]. Inorganic contaminations are absorbed by the stack's MEAs and lead to a loss of protonic conductivity [24,25].

In the literature, numerous studies address the problem of contamination-based aging processes in DMFCs. For instance, Zhao et al. [26] show that even a small amount of chloride anions in the fuel of a DMFC can cause a significant loss in cell performance. Yasuda et al. [27] investigate the effects of inorganic impurities (e.g., aluminum, iron, nickel and sodium) and possible organic fuel contamination in the form of methyl formate, acetic acid, ethanol, acetone, 1-propanol and 2-propanol on the performance of a fuel cell. The effects of sodium and ethanol are also reported by Nishimura et al. [28]. Jie et al. [29] systematically investigate in situ the effects of different valency cations (Na^+, Mg^{2+} and Cr^{3+}) on DMFC performance. All the articles indicate the necessity of avoiding inorganic impurities in a DMFC system, since in many cases it is the strongest degradation effect in a DMFC system.

In recent years, organic impurities were effectively avoided in the DMFC systems that were developed and operated at the IEK-3. We achieved this by only using methanol of a suitable quality and avoiding peripheral components in the DMFC systems that are not resistant to the prevailing operational conditions. On the other hand, inorganic impurities are present in the system's anodic cycle, although very resistant components and materials have been used. The concentration of cations that were found in the anodic cycle of one of our DMFC systems was systematically investigated by Kimiaie et al. [30]. In particular calcium could be detected in elevated concentrations, along with traces of aluminum, potassium, sodium, nickel and chromium. Kimiaie investigated the sources for the detected inorganic impurities and came to the result, that the system's components are a minor source for impurities. Especially the very high amount of calcium detected is emitted by the bipolar-plates. Within the stack design developed at the IEK-3, a flexible but porous graphite material with the trade name Sigraflex® of the company SGL Carbon is used. This material has advantages regarding manufacturing aspects, but due to its porosity and its enlarged surface, the anodic solution washes out bounded contaminations. This effect is a disadvantage of the material, but since we showed a lifetime of 20,000 operating hours, the material is acceptable for the use in bipolar-plates.

Park et al. [13] propose the use of *ion exchange resins* (IERs) in the anodic cycle of DMFC systems in order to avoid inorganic impurities. On the basis of this suggestion, Kraus et al. [31] carried out simulations to investigate how an anion exchanger can be implemented in a DMFC system. Till now however, no publications have reported on the characterization of materials to investigate the viability of ion exchangers in DMFC systems, nor whether there are stable materials under prevailing operating conditions.

This paper outlines a material screening to qualify IERs for use in a DMFC system. On the one hand, it investigates, whether IERs are chemically stable at elevated temperatures in a methanol water solution, in order to ensure that no additional impurities have been emitted. On the other, the activity as well as the capacity of the materials was tested by flushing a contaminated solution through an IER cartridge and measuring the outlet concentration of inorganic impurities.

By evaluating the results, the most suitable materials could be identified. The results provide a database for the design of IER cartridges that fits the requirements of DMFC systems. In general, if the emission of ions over the operating time is known, it is possible to design an IER cartridge for the lifetime of a DMFC system with a certain capacity for ionic contaminations. The emission of ionic contaminations can be estimated by analyzing the contaminations bound in the MEAs