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Statistical investigations of basis weight and thickness distribution of continuously produced fuel cell electrodes

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HIGHLIGHTS

- The knife coating process for electrode production is investigated.
- Investigation of electrode basis weight distribution indicates coating defects.
- A construction fault in the coating machine causes a gradient in the catalyst layer.
- Variance of catalyst basis weight is determined by properties of the substrate used.

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ABSTRACT

The presented work is focused on the investigation of catalyst basis weight scattering in direct methanol fuel cell electrodes produced by a roll-to-roll process. For the manufacturing of highly efficient electrodes the statistical variance of the catalyst basis weight should be as small as possible.

The dependencies between the variances of the catalyst basis weight, substrate basis weight, substrate thickness, and electrode basis weight are inferred from theoretical considerations. A commercial substrate is coated with catalyst dispersion by a continuous knife coating process to manufacture the electrodes. The basis weight and thickness of the substrate and the electrode are investigated ex-situ. The distribution of the measurands enables the determination of an estimator for the expected value and the variance which are used to calculate the variance of the catalyst basis weight.

The main finding of the investigations is that different impacts on the distribution of the catalyst basis weight exist. A construction fault in the coating knife of the employed coating machine causes a gradient in the catalyst layer. After removing this fault it can be proved that a periodic structure in the substrate basis weight and thickness is responsible for a large contribution to the catalyst basis weight variance.

1. Introduction

Over the last few years, a number of direct methanol fuel cell (DMFC) prototype systems have been developed [1,2]. They are interesting for many applications, such as battery replacement in mobile electronic, fork lifts, or uninterruptible power supplies [3,4]. Though some systems fulfill the requirements of longevity they are still very expensive in comparison to well-established systems, such as battery systems [5]. One strategy to reduce the investment and operating costs of fuel cell systems is to increase the electrical efficiency.

The efficiency of a DMFC system is primarily determined by the membrane electrode assemblies (MEAs). They must be able to convert the chemical energy of methanol to electrical energy with maximum efficiency, maximum power density, and with as little expensive catalyst as possible. To achieve these apparently conflicting requirements, it becomes necessary to find appropriate production processes and materials for the manufacturing of the electrodes which are important subcomponents of the MEA.

The processes and materials are generally tested and developed in laboratory scale [6,7]. Small amounts of material and laboratory equipment are used for the discontinuous production of test electrodes to investigate physical and electrochemical correlations. If appropriate processes and materials are identified, the processes must be scaled up for the pilot plant production. For this scale-up it is essential that the large-sized electrodes have uniform physical properties over the entire active area.

One important electrode property is the catalyst basis weight. The higher the catalyst basis weight the higher the cell voltage, and gradients in cell voltage are able to affect the electrode efficiency

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[8]. Some research has been done to find the optimal catalyst distribution in a catalyst layer [9–11] without considering the fact that every production process generates an undesired distribution with a specific variance. The homogeneity of the catalyst basis weight is of particular attention for the production of large-sized fuel cell electrodes.

The characterization methods for large-sized electrodes can be classified as in-situ and ex-situ methods. The industrial production of uniform stack electrodes requires in-situ methods to control substrate and electrode properties during the production [12]. The main emphasis of this study is research and development of the production processes. In this case, ex-situ methods are more suitable because existing measurement devices can be further developed in an easier way than on-line measurement devices in a production machine.

One core task of the presented work is the manufacturing of homogeneous square meter sized electrodes for direct methanol fuel cells. The electrodes are produced by using a knife coating process for the direct coating of gas diffusion layers with catalyst dispersion. One advantage of this process is the option to produce either small or large electrodes which is important for research and development. Another advantage is the scalability from laboratory to pilot plant scale which is a crucial aspect for the production of large-sized electrodes.

A challenge of the direct coating of dispersions on a porous substrate is the complex interdependency between the substrate and the dispersion. The substrate properties, such as thickness, wetting behavior, and pore size distribution have a direct influence on the structure of the coated layer. Effects like dispersion penetration in the substrate, which is also affected by the rheological properties of the dispersion, can lead to a reduced quality of the electrode. More fundamental research is necessary to understand the complex interdependencies between a porous substrate and a non-Newtonian dispersion.

With regard to the variance of the catalyst basis weight of continuously manufactured electrodes no measured data can be found in literature. Additionally, no systematic investigations of the basis weight or thicknesses distribution of substrates are available. Therefore, the basis weight and thickness distribution of the commercial substrate used and the produced electrodes are statistically analyzed by using an ex-situ method.

The aim of the presented work is the manufacturing of uniform electrodes, the determination of estimators for the statistical expected value and for the variance of the catalyst basis weight. In relation to these estimators the produced electrodes are judged, and different influences between the electrode production process and the variance of the catalyst basis weight are investigated. The challenge is to decrease the variance of the catalyst basis weight in order to increase the electrode efficiency.

2. Experimental

The following sections present a survey about the applied production and investigation techniques in this work. The different challenges are explained, and the relevant equations for the calculation of the catalyst basis weight variance are introduced.

2.1. Electrode production

The first step in electrode production is the in-house preparation of catalyst dispersion with specific catalyst content in the solid phase (ω_{cat}). The dispersion is coated on a substrate by using a knife coating process [13]. After the coating is applied, the electrode is dried, and the mass can be measured to determine the electrode basis weight. For the determination of the electrode catalyst loading the basis weight of the substrate is needed. The calculation of the catalyst basis weight for a discontinuously produced laboratory electrode is different in comparison with a continuously manufactured pilot plant electrode. This difference is described in the following sections.

2.1.1. Discontinuous electrode production in laboratory scale

For the electrode production in laboratory scale a sample of the substrate is cut out from a substrate roll with the size of the needed electrode. The mass (m_s) and the area (A) of the sample are measured, and the basis weight of the substrate (bw_s) is calculated. In laboratory experiments electrodes with an area of 4.2 cm × 4.2 cm are used. The basis weights of these small samples can be determined very precisely before the coating.

With the assistance of a mask the sample is coated with the catalyst dispersion by a lab coater. After drying, the mass of the electrode (m_e) is measured, and the basis weight of the electrode (bw_e) is determined. Fig. 1 shows the different steps for electrode production in laboratory scale.

The catalyst mass fraction (ω_{cat}) in the solid content of the dispersion is a function of the dispersion composition, and it is needed to calculate the catalyst basis weight of the electrode.

$$bw_{cat} = \omega_{cat} \times (bw_e - bw_s) \quad (1)$$

In case an unknown substrate or a new dispersion is used for the electrode production, laboratory preliminary tests have to answer the question whether or not the substrate can be coated with the dispersion or which adjustments for the coating process are necessary. Furthermore, rheological investigations of the dispersion can help to detect coating problems in advance before the electrodes are produced with the pilot plant.

Currently, the results from laboratory experiments are not fully transferable to the pilot plant production. For example, the catalyst basis weight of a produced laboratory electrode and a pilot plant electrode can be different, even though the same parameter values are used for the manufacturing. Therefore, to produce an electrode with a specific desired catalyst loading, the right adjustment of the knife height (kh, see Section 2.1.3) must be determined in the pilot plant by a calibration experiment. This experiment is described in Section 3.2.

2.1.2. Continuous production of stack electrodes in pilot plant scale

For the manufacturing of stack electrodes with a pilot plant the substrate is initially unrolled from a roll. Afterward, the electrode is

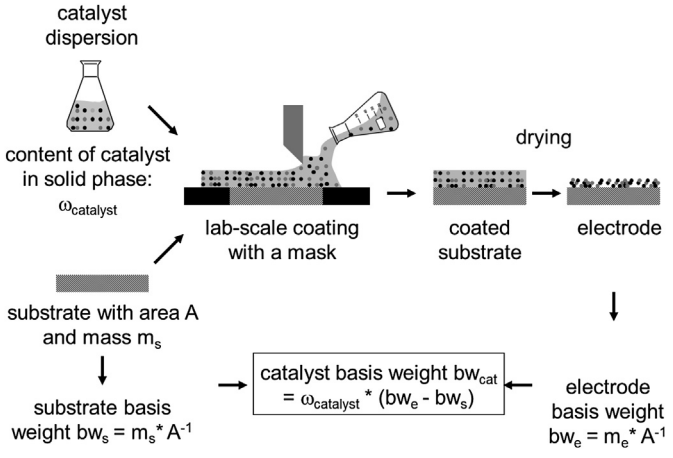

Fig. 1. Schematic representation of the electrode production in laboratory scale. The basis weight of the coated substrate is determined before the coating, and together with the basis weight of the electrode the catalyst loading can be calculated.