Journal of Power Sources 327 (2016) 526–534

Contents lists available at ScienceDirect

Journal of Power Sources

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

Analyzing the influence of high electrode potentials on intrinsic properties of catalyst coated membranes using impedance spectroscopy

Robert Alink*, Martina Schüßler, Maximilian Pospischil, Denis Erath, Dietmar Gerteisen

Fraunhofer Institute for Solar Energy Systems ISE, Germany

HIGHLIGHTS

- Maximum catalyst layer performance found with 31–34 wt% ionomer content.
- New impedance transition line model including interfacial CCM properties.
- Low performance of low ionomer catalyst layer due to high interface resistance.
- 1.3 V electrode potential improves performance of low ionomer loading catalyst layer.
- Catalyst layer proton conductivity is improved by high electrode potentials.

ARTICLE INFO

Article history:
Received 17 May 2016
Received in revised form
21 July 2016
Accepted 22 July 2016
Available online 30 July 2016

Keywords:
PEM fuel cell
Catalyst layer
Ionomer content
Aging
Impedance spectroscopy
Interface resistance

ABSTRACT

Catalyst layers (CLs) with varying ionomer contents are produced using a stencil coating and screen printing technique. The optimum ionomer content of 31–34 wt% confirms the findings of other groups and performance is found to be independent of production technique. A new CL impedance transition line model is developed and fitted to in-situ data. The results indicate that the protonic contact resistance between CL and membrane is an important factor for the used transfer-decal process, especially for CLs with low ionomer loading.

When subjected to potentials higher than 1.2 V, an increased performance is observed for low ionomer loading CLs. It is found that by applying the high potential to the electrode a significantly increased proton conductivity is counteracting and superimposing the loss of electrochemical surface area (ECSA) due to carbon corrosion. After aging, the performance of the 15 wt% CL is at the same level as the 31–34 wt% ionomer content CLs at the beginning of life, even though the ECSA is reduced due to carbon corrosion or platinum dissolution. The findings indicate that for the optimization of the ionomer loading, either the changing wetting properties or the redistribution of ionomer during lifetime have to be taken into account.

1. Introduction

In catalyst layers (CLs) of Polymer Electrolyte Membrane (PEM) fuel cells, the ionic connection between the ionomer membrane and the catalytically active sites is a key factor for performance, durability and efficiency. Highly dispersed ionomer is used both as a mechanical binder and a proton conductor between the catalyst particles, the carbon support and the membrane. The distribution and the structure of the ionomer significantly determines losses due to proton transport from the membrane to the electrochemically active sites as well as reactant diffusion losses. A comprehensive review on catalyst layer ingredients and fabrication methods has recently been given by Zamel [1].

A number of publication have shown that an optimum in CL ionomer content exists, which is dependent on catalyst and support material as well as production methodology [2–5]. The reason behind the existence of an optimum is by the conflicting interest between maximum proton conductivity and minimum reactant concentration losses. The reactant concentration losses are induced by diffusion processes which increase with ionomer content in the

* Corresponding author.
E-mail address: robert.alink@ise.fraunhofer.de (R. Alink).

http://dx.doi.org/10.1016/j.jpowsour.2016.07.084
0378-7753/

CL. Newer findings indicate that in up-to-date CLs the active sites are fully covered with an ionomer film [6,7] and the reactants have to dissolve and diffuse through the film to reach the active sites. Liu et al. found that the ionomer network is well established with a tortuosity of approximately 1 for ionomer to carbon ratios (I/C) higher than 0.6/1 [7]. On the other hand, for low ionomer loadings, kinetic voltage losses attributed to low humidity operation at 36% *RH* is lower than 25 mV whereby losses due to proton conduction in the CL can be as large as 200 mV [7]. Different experimental studies have revealed that an optimum I/C ratio lies between I/C = 1.0 (30 wt% ionomer) for a 57 wt % Pt catalyst [5], 0.7–1.2 for a 40 wt% Pt catalyst [8], 0.5 [3] or 0.6 (30–33 wt% ionomer) [2,9] for a 20 wt% Pt catalyst or 1 mg cm^{-2} for a catalyst loading of 0.5 mg cm^{-2} [4].

To understand the physics behind the optimization of the ionomer content and distribution in the CL, information about the ionomer structure in the final layers is a key factor. In recent time, different approaches have attempted to visualize the internal structure of the CL, in particular the distribution of the ionomer and platinum [6,10–15]. However, some questions on the validity of the approaches remain and the methods are excessively extensive to be applied in an optimization process for the CL production. A promising method to access the intrinsic properties of the catalyst coated membranes is by electrochemical impedance spectroscopy (EIS). Publications have shown that the high frequency region of the impedance contains information on the CL structure and properties that reveal important insights for catalyst layer optimization. Often, the spectra are recorded with nitrogen on the cathode to suppress the electrochemical reaction which interferes with the signal containing the structural properties of the CL. Mostly, the 45° branch in the high frequency part is analyzed to extract the proton conductivity of the CL [2,7,16–20]. To monitor the influence of aging on the catalyst layer, the 45° arc has been analyzed during life time testing by different groups [17,21,22].

In this work, the production method and ionomer content of catalyst coated membranes (CCMs) is varied and evaluated using current voltage curves to find an optimum for the ionomer loading in terms of maximum fuel cell power output. Impedance spectra are recorded and analyzed by modeling to determine the intrinsic CL properties. A new catalyst layer impedance model is developed and fitted against the impedance data, giving the proton resistance and capacitance of the bulk catalyst layer and the interface to the membrane as a function of ionomer content. After, an accelerated stress test is applied to test the effect of high potentials on the performance and structural properties of the tested materials.

2. Experimental

2.1. CCM fabrication

A homogenous suspension composed of platinum on carbon (40 wt% Pt-C, Quintech), Nafion™(POW Dion-40 + 60 mesh, Ion Power) and a mixture of organic solvents (ethylene glycol, propylene glycol propyl ether) was prepared. Nafion™ was dissolved in the solvent mixture and the catalyst powder was added. The suspension was homogenized by stirring and ultra-sonication. Suspensions with varying Nafion™ionomer content were prepared with 15, 20, 25, 31 and 34 wt% ionomer content in dry layers.

The catalyst layers were formed on a transfer foil (Teflon) by stencil coating and dried on a hotplate at 80°C with an area of 6 × 6 cm^2. Moreover, CLs were prepared by screen printing. To achieve a sufficient layer thickness a threefold printing process was performed. To determine the CL thickness, cross sections of the CLs were prepared and analyzed by SEM imaging. The (wet) thickness of the CLs remained the same during all experiments, resulting in a varying platinum loading for the different ionomer loadings. The final platinum loading was determined by weighting dry samples. Table 1 lists the mean value and standard deviation of the CL dry thickness as well as the platinum loading.

The catalyst layers are transferred onto a Gore-Select® membrane M735.18 (18 μm thickness) and compressed at 1.25 MPa, 140°C for 5 min.

The break-in procedure is realized by operating the cell at the same conditions as the polarization curve. The cell is operated at 0.6, 0.5, 0.4 and 0.3 V for 5 min before it is 10 times cycled (stepwise) between 0.2 V (30 min) and 0.8 V (1 min).

2.2. In-situ characterization

The CCMs are assembled in a baltic FuelCells quickConnect®test cell with a 5-fold serpentine flow field. The active area is 5 × 5 cm^2, the channel and rib width is 0.5 mm respectively and the cell compression is set to 157 N cm^{-2} on the flow field lands at atmospheric back pressure. All experiments are recorded with constant gas flow and full humidification (dew point 80°C) using bubbler humidifiers, while the cell temperature is controlled to 80°C.

Polarization curves are recorded galvanostatically beginning from the current at 200 mV to open circuit voltage. The air/hydrogen pressure is set to 2.5 *bara* at the cell outlets and a constant mass flow of 3/2 l min^{-1}, corresponding to a stoichiometry of 2.4/3.8 at 3 A cm^{-2} on cathode/anode is used. After the cell temperature is constant between 79 and 81°C, each current step is kept constant for 10 min for current densities above 0.2 A cm^{-2} and 5 min below 0.2 A cm^{-2}, before the data is recorded over 2 min.

After recording the polarization curve, the cell is purged with nitrogen on the cathode for 20 min before cyclic voltammograms (CVs) and the impedance spectra are recorded. 2 × 5 CVs are recorded with a scan rate of 20 mVs^{-1} at 100 ml min^{-1} hydrogen and 100 ml min^{-1} nitrogen flow rate. For the calculation of the electrochemical surface area (ECSA), a horizontal line is fitted to the current/voltage data between 400 and 500 mV and the current in the hydrogen adsorption region is integrated between 170 and 400 mV. The lower limit of 170 mV is chosen according to the minimum in measured current, according to Carter et al. [23]. Impedance Spectra are recorded directly after the CVs with 500 ml min^{-1} nitrogen on the cathode and 100 ml min^{-1} hydrogen on the anode at a DC-potential of 100 mV. The frequency is scanned from 10 kHz to 1 Hz with an amplitude of 10 mV.

2.3. CCM model and data fitting

To model the 45° high frequency impedance arc, a classical spatially resolved transition line model of a porous electrode is used in which one resistance rail represents the electronic and one rail the protonic phase [2]. The charge transport is modeled using a high number of parallel resistors and capacitances representing the double layer capacitance, the charge transfer resistance and the ohmic proton resistance in the CL (see Fig. 1). The electron resistance of the CL is neglected due to the significantly higher resistance of the protonic phase. Using such a model, the AC signal penetration depth into the CL varies with frequency, resulting in a 45° branch for frequencies between approximately 100 Hz and 10 kHz if assuming homogeneously distributed properties. If an inhomogeneous distribution of the proton conductivity or the double layer capacitance in the through-plane direction is assumed, Gerteisen found in his modeling work that the straight 45° line bends to form a high frequency arc [18]. The resulting high frequency semicircle has been found before in experiments [24–26] but the underlying phenomena have not yet been fully understood. It was speculated that it is due to structural features of the membrane electrode assembly [24], inhomogeneous capacitance or