Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Power Sources 145 (2005) 407–415
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

Statistic analysis of operational influences on the cold start behaviour of PEM fuel cells

M. Oszcipok*, D. Riemann, U. Kronenwett, M. Kreideweis, M. Zedda

Fraunhofer Institute for Solar Energy Systems, Germany

Accepted 2 February 2005
Available online 29 April 2005

Abstract

For portable fuel cell systems a multitude of applications have been presented over the past few years. Most of these applications were developed for indoor use, and not optimised for outdoor conditions. The key problem concerning this case is the cold start ability of the polymer electrolyte membrane fuel cell (PEMFC). This topic was first investigated by the automotive industry, which has the same requirements for alternative traction systems as for conventional combustion engines.

The technical challenge is the fact that produced water freezes to ice after shut-down of the PEMFC and during start-up when the temperature is below 0 °C.

To investigate the basic cold start behaviour isothermal, potentiostatic single cell experiments were performed and the results are presented.

The cold start behaviour is evaluated using the calculated cumulated charge transfer through the membrane which directly corresponds with the amount of produced water in the PEMFC. The charge transfer curves were mathematically fitted to obtain only three parameters describing the cold start-up with the cumulated charge transfer density and the results are analysed using the statistical software Cornerstone 4.0.

The results of the statistic regression analyses are used to establish a statistic-based prediction model of the cold start behaviour which describes the behaviour of the current density during the experiment. The regression shows that the initial start current mainly depends on the membrane humidity and the operation voltage. After the membrane humidity has reached its maximum, the current density drops down to zero. The current decay also depends on the constant gas flows of the reactant gases.

Ionic conductivity of the membrane and charge transfer resistance were investigated by a series of ac impedance spectra during potentiostatic operation of the single cell at freezing temperatures. Cyclic voltammetry and polarisation curves between cold start experiments show degradation effects by ice formation in the porous structures which lead to significant performance loss.

Keywords: PEMFC; Cold start; Statistic analysis; Impedance spectroscopy; Cyclic voltammetry; Degradation

1. Introduction

Sub zero temperature operation of portable fuel cell systems is a relatively new topic and not much literature is published. Cargnelli et al. operated a 50 W PEMFC system in a climatic chamber at −42 °C and used for the start-up a catalytic burner to heat up and humidify the reaction air [1]. Chu et al. operated a 50 W fuel cell system at −10 °C for 9 h [2]. Datta and Velayutham reports of a 500 W fuel cell system which was operated without any problems in the Antarctic [3].

More fundamental in situ investigations of non-isothermal, galvanostatic single fuel cell experiments below 0 °C were performed by Kagami et al. At constant gas flow it is described that the cathode electrode surface is reduced by ice formation and therefore the reaction is inhibited. With the empirical assumption that the cathode surface is diminished proportional with the amount of frozen water, simulations were done which describe the voltage decay over time in

* Corresponding author. Tel.: +49 761 4588 5432; fax: +49 761 4588 9432.
E-mail address: michael.oszcipok@ise.fraunhofer.de (M. Oszcipok).

0378-7753/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2005.02.058

Nomenclature

BET	Brunauer–Emmett–Teller porosity analysis
c	exponent variable, constant
CV	cyclic voltammetry
EDS	energy dispersive X-ray spectroscopy
F	Faraday constant (96485 C mol^{-1})
GDL	gas diffusion layer
i	current density (mA cm^{-2})
$i_{\text{linear,start}}$	current density at start of slow decrease (mA cm^{-2})
i_{peak}	peak current density during cold start (mA cm^{-2})
i_{start}	current density at initial cold start (mA cm^{-2})
MEA	membrane electrode assembly
$m_{\text{H}_2\text{O,prod}}$	area specific product water (g cm^{-2})
$M_{\text{H}_2\text{O}}$	molar weight of water (g mol^{-1})
MPL	microporous layer between electrode/GDL
p	influence parameter in regression polynomial
p_{450}	reference power density at 450 mV (mW cm^{-2})
R^2	stability index
R^2_{adj}	adjusted stability index
R_{ct}	charge transfer resistance from Nyquist plot (mΩ cm^2)
$R_{\text{m,c}}$	membrane/contact resistance from Nyquist plot (mΩ cm^2)
SEM	scanning electron microscopy
$S_{\text{q,cum}}(t)$	cumulated charge transfer density (C cm^{-2})
$S_{\text{q,fit}}$	fitted cumulated charge transfer density (mC cm^{-2})
$S_{\text{q,max}}(t)$	max. cumulated charge transfer density (C cm^{-2})
$S_{\text{q,peak,end}}$	cum. charge transfer density at end of peak (mC cm^{-2})
$S_{\text{q,peak,start}}$	cum. charge transfer density at start of peak (mC cm^{-2})
t_{63}	time when $S_{\text{q,fit}}(t)$ reaches 63% of $S_{\text{q,max}}$ (min)
u_{air}	air flow rate (ml min^{-1})
V	voltage (mV)
V_{OC}	open circuit voltage (mV)
x_{i}	value of influence parameter
y	response variable in regression polynomial
Z_{start}	Impedance at 1000 Hz before cold start-up (mΩ)

good correlation with experimental results. Beneficial for the cold starts are low current densities which prevent voltage decay by freezing of product water [4,5].

In this paper we present the results of potentiostatic single cell cold start-up measurements under isothermal conditions at −10 °C. The current density is increasing very fast after initial start-up and later it decays towards zero. This behaviour is ascribed to freezing of product water in the cathode. To find out the main influencing operational parameters on the cold start behaviour, statistic methods are used. Finally, a statistic-based prediction model of the current decay during isothermal cold start was developed.

To get a deeper insight into the dynamic processes in the cathode during cold start-up dynamic electrochemical impedance spectroscopic analyses were done, which show that the membrane/contact resistance as well as the charge transfer resistance is changing with the amount of produced water.

Impedance spectroscopy at 80 °C was also used by Cho et al. to find out changes of single fuel cell characteristics by ex situ thermal cycling. The author concludes that the contact resistance in the fuel cell is increasing after thermal cycles because of worse contact between the membrane and the electrode, whereas the membrane ionic conductivity itself is not affected [6]. The impact of ex situ thermal cycling on the degradation of Nafion® membranes was examined by McDonald et al. It is reported that the ionic conductivity and the mechanical properties are hardly changing. However, opening up of the molecular structure of the polymer in connection with enlargement of hydrophilic areas was found [7]. Cappadonia et al. investigated Nafion® membranes by thermal cycling and it was found that two different water environments exist below 0 °C. Water phase transition depends on the water content in the membrane. Higher water contents lead to larger pore diameters in the membrane and therefore to a lower freezing temperature of water. In water-rich samples phase transitions were observed at 260 K [8].

Nevertheless, performance degradation can be observed, as described in [6,9]. A degradation rate of about 2.8% at 80 °C and 0.6 V per-freeze-thaw cycle down to −10 °C is observed as well as a reduction of about 6% per thermal cycle of the electrochemical active surface area of the cathode. It was found that the pore size distribution in the electrode changes to larger pores by thermal cycles.

Our measurements with cylic voltammetry (CV) also show degradation of the cathode electrode surface by isothermal sub zero operation, and furthermore changes in hydrophobicity of both, the microporous layer (MPL) and the gas diffusion layer (GDL) on the cathode side. We finally also found performance degradation at 450 mV and 30 °C of more than 5% per each cold start experiment.

2. Experimental and results

2.1. Maximum cumulated charge transfer density

The cold start experiments were carried out with a single cell with an active area of 46 cm^2. The flowfield had a double serpentine structure and the cell assembly was done using commercial standard components consisting of GDL, MPL and catalyst-coated membrane.