Journal of Power Sources 269 (2014) 344–362

Contents lists available at ScienceDirect

Journal of Power Sources

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

Study of low concentration CO poisoning of Pt anode in a proton exchange membrane fuel cell using spatial electrochemical impedance spectroscopy

Tatyana V. Reshetenko [a,*], Keith Bethune [a], Miguel A. Rubio [b], Richard Rocheleau [a]

[a] Hawaii Natural Energy Institute, University of Hawaii, 1680 East-West Road, POST 109, Honolulu, HI 96822, USA
[b] Departamento de Informática y Automática, UNED, Juan del Rosal 16, 28040 Madrid, Spain

HIGHLIGHTS

- The effects of CO on spatial PEMFC performance and EIS were studied with a segmented cell.
- The experiments were performed using various cathode gases: air, O_2 and H_2.
- Injection of CO resulted in a voltage decrease and redistribution of segments' currents.
- The spatial EIS data were analyzed using the equivalent electric circuits approach.
- A current distribution model and EIS interpolation method were applied for detailed analysis.

ARTICLE INFO

Article history:
Received 22 April 2014
Received in revised form
25 June 2014
Accepted 26 June 2014
Available online 7 July 2014

Keywords:
PEMFC
Pt anode
Carbon monoxide poisoning
Spatial EIS

ABSTRACT

This paper presents experimental and modeling results of the effect of low CO concentration (2 ppm) on the spatial performance of PEMFC as well as its spatial electrochemical impedance spectroscopy (EIS) responses. The cell was operated at constant current using various cathode gases: air, O_2 and H_2. Due to CO adsorption on the Pt anode and its poisoning, the cell voltage decreased and spatial current redistribution was observed. The steady state voltage losses were 0.089, 0.280 and 0.295 V for the H_2/O_2, H_2/air and H_2/H_2 gas configurations, respectively. EIS data revealed a pseudo-inductive behavior in the low frequency region for inlet segments of the cell operated under H_2/air and H_2/H_2 conditions. Operation with O_2 as an oxidant did not cause any pseudo-inductance. Analysis of the EIS and anode overpotential data suggested that CO oxidation occurred via chemical or electrochemical mechanisms, or a combination of both depending on the selected cathode gas. The spatial EIS data were analyzed using the equivalent electric circuits approach. The distributions of the equivalent electric circuit parameters are presented and discussed. A current distribution model and EIS interpolation technique were successfully applied for detailed analysis of CO effects on the spatial PEMFC performance and EIS.

1. Introduction

Fuel cells are receiving increasing attention due to their high energy conversion rates and harmless emission products as well as their promising future applications for powering stationary and portable devices and electric vehicles [1]. The highest performance is achieved with H_2, which is the preferred fuel for low temperature proton exchange membrane fuel cells (PEMFCs). However, the application of H_2 as a fuel for PEMFCs has several limitations, predominantly due to current methods of H_2 production which commonly occurs via the stream reforming of natural gas [2,3] as well as water electrolysis. Focusing on the reforming processes, a by-product of these is carbon monoxide. To minimize the CO content, several additional stages are incorporated into the reforming process, namely the water gas shift reaction and low temperature preferential oxidation. The resulting CO concentration is in the range of 10–50 ppm. However, even a low CO content can significantly reduce the performance of fuel cells [4–17]. Recent standards released specifying acceptable hydrogen gas compositions for fuel cell applications set the maximum CO concentration at 0.2 ppm in attempt to alleviate concerns of contamination (ISO

* Corresponding author. Tel.: +1 808 593 1714; fax: +1 808 593 1719.
E-mail addresses: tatyanar@hawaii.edu, t_reshetenko@mail.ru (T.V. Reshetenko).

http://dx.doi.org/10.1016/j.jpowsour.2014.06.146

14687-2, SAE J2719). The main reason for the performance loss due to CO contamination in PEMFCs is the preferential adsorption of CO on Pt sites, which leads to the inhibition of H_2 dissociative adsorption and its further oxidation. Several approaches have been proposed to mitigate the effect of CO on PEMFCs. These approaches include preventative measures by reducing carbon monoxide concentrations through current advances in preferential CO oxidation techniques and the water gas shift reaction [1–3,18], and in-situ techniques such as the pulsed oxidation of a CO poisoned electrode [19,20], air bleeding into a H_2 stream [3,4,13,21–25], the use of CO-tolerant catalysts [7,10,11,23,26,27], and/or operation under particular conditions (high temperature, pure H_2 pulsing, high cathode back pressure) [28–31].

For the diagnosis of fuel cell performance, electrochemical impedance spectroscopy (EIS) is a well-established method [32–35]. The method is based on a small sinusoidal perturbation of the electrochemical system (either in current or voltage) and measurement of the response signal. Because of the small amplitude of the perturbation, the system is assumed to be linear in the range of perturbation, and the linear impedance is analyzed. Variation of the perturbation frequency allows processes with different time constants to be separated. EIS has been applied for the investigation of various phenomena in PEMFC: dehydration, flooding and poisoning by impurities including CO.

The first in-situ measurements of CO poisoning with EIS were published by B. Müller [36] and M. Ciureanu [37]. The paper [36] reported the time dependence of impedance spectra under galvanostatic conditions and CO exposure of the Pt anode, while potentiostatic electro-oxidation of H_2/CO was studied in Ref. [37]. It is useful to operate the fuel cell in the galvanostatic mode because a constant current density means a constant reaction rate. Additionally, the impedance of the membrane and cathode might also be assumed to be constant, and any observed differences in EIS profiles can be attributed to changes in the anode impedance. Several other publications also present detailed EIS data concerning the effect of CO on H_2 oxidation at the anode [38–50]. It was demonstrated that the CO poisoning of Pt-containing anodes caused an increase of the total impedance of a cell. The impedance response strongly depended on the exposure time, potential, CO concentration, temperature, and oxygen crossover. An occurrence of a pseudo-inductive loop was detected at low frequency under certain conditions. The loop was observed to be related to the surface relaxation of the anode. Furthermore, the effect of CO on the electrochemical behavior of the fuel cell can be interpreted using the Faraday impedance in addition to the potential-dependent hindrance of the charge transfer [36,38–40,43,46,51–53]. Progressive poisoning with CO of a fuel cell during EIS measurements can complicate the analysis of the data because the examined system should be at steady-state when EIS is running. However, violation of steady-state conditions often occurred, and to solve these problems, time-resolved EIS (TREIS) was introduced [54].

The use of H_2 fuel containing low levels of CO is likely to cause a varying distribution of Pt sites occupied by CO, thus creating areas with low performance located mainly at the inlet of the cell, leading to the redistribution of local/spatial currents and affecting the spatial impedance responses. Therefore, EIS of the cell under CO exposure depends not only on the time of exposure but also on the location inside the membrane electrode assembly (MEA). The evaluation of fuel cell performance with a single cell approach only provides an average of the local voltage, current, and impedance values and does not reveal the spatial behavior of the cell. A segmented cell system is a powerful tool for understanding the details of locally resolved fuel cell processes [55]. There are many examples of segmented cell research applications in PEMFC studies, including basic investigations of local current distributions [56–60], gas and water management effects [61–65], stack and single cell diagnostic techniques [66–69], defect detection and localization methods [70–74], recirculation [75], start-up, and starvation impact [76–79]. However, there are only a few papers devoted to using segmented cells with poisoned electrodes [16,17,22,30,80]. The authors of these publications discussed the redistribution of the local currents under CO poisoning at relatively high concentrations on the order of 50 ppm up to 3%. Our previous paper [6] presented results concerning the effect of low concentration CO (2 ppm) on PEMFC spatial performance under galvanostatic conditions (0.8 A cm^{-2}) and H_2/H_2, H_2/air and H_2/O_2 gas configurations for the anode/cathode. In that paper, spatial EIS data presented the dynamic responses of the segments upon CO exposure and revealed pseudo-inductance at low frequency and an increase not only in the anode charge transfer resistance but also in the cathode charge transfer resistance. This paper is a continuation of our studies and focuses on detailed spatial EIS characterization of PEMFCs during low CO concentration exposure (2 ppm). The selected CO concentration is still 1 order of magnitude higher than current H_2 fuel cell commodity gas specifications, but in comparison to other studies mentioned is quite low and for the purposes of this analysis may be considered to more closely represent the real operating conditions for PEMFCs. Moreover, a mathematical model describing the temporal evolution of the spatial current densities was adapted and expanded; results are presented and discussed to help further interpretation of the experimental observations.

2. Experimental

All the experiments were conducted on a single cell test station using Hawaii Natural Energy Institute's (HNEI) segmented cell system, which enables the simultaneous acquisition of spatially distributed data [68]. The segmented cell approach for this study builds upon the works of Cleghorn et al. [56], the German Aerospace Centre, Stuttgart [81], Ballard Power Systems Inc. [57], and Los Alamos National Laboratory (LANL) [82]. HNEI's segmented cell system is partially based on the LANL design using closed loop Hall sensors and an improved data acquisition system. These enhancements allow the system to perform simultaneous rather than sequential measurements of spatial EIS, spatial linear sweep voltammetry (LSV), and cyclic voltammetry (CV). The segmented cell hardware is based on the HNEI 100 cm^2 cell design. The hardware contains a segmented anode flow field consisting of ten consecutive segments disposed along the path of a ten-channel serpentine flow field. Each segment has an area of 7.6 cm^2, with its own distinct current collector. The same channel designs are used for both the segmented anode and the standard cathode flow fields (the reactant streams were arranged in a co-flow configuration).

The segmented cell system consists of the cell hardware, the current transducer system, the data acquisition device and a single cell test station. The current transducer system was custom designed. A closed loop Hall sensor (Honeywell CSNN 191) is employed for current sensing. For EIS measurements these sensors show very little inductance over the entire frequency range of interest. The system allows the investigation of as many as 10 current channels in a high (standard) current mode and 16 channels in a low current mode. The standard current mode enables the measurement of segment currents up to 15 A. The current limit of the data acquisition system can be extended to 30 A or more using a unique counter current technology that allows a flexible segmented cell design, high current operation and increased accuracy during EIS experiments. The low current mode of the system yields current measurement up to 375 mA, with an accuracy of ±2.5%, which is a