Journal of Power Sources 247 (2014) 40–48

Contents lists available at ScienceDirect

Journal of Power Sources

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

Influence of cell temperature on sulfur dioxide contamination in proton exchange membrane fuel cells

Y. Zhai*, G. Bender [1], K. Bethune, R. Rocheleau

Hawaii Natural Energy Institute, University of Hawaii, Honolulu, HI 96822, USA

HIGHLIGHTS

- Lower temperature, less performance recovery was obtained by neat air operation.
- Full recovery was obtained by CV scanning after contamination at low temperature.
- Increase of liquid water in MEA delayed the poisoning process at low temperature.
- Decomposition/desorption of sulfur adsorbates was inhibited at low temperature.
- SO_2 crossover from cathode to anode was also mitigated at low temperature.

ARTICLE INFO

Article history:
Received 11 June 2013
Received in revised form
5 August 2013
Accepted 12 August 2013
Available online 30 August 2013

Keywords:
PEM fuel cell
Sulfur dioxide contamination
Electrochemical impedance spectroscopy
Cyclic voltammetry
Water balance

ABSTRACT

The effects of temperature on sulfur dioxide (SO_2) contamination in PEMFCs are investigated by operating single cells with 2 ppm SO_2 in the cathode at different temperatures. Cell performance response shows that voltage degradation was delayed and appears a transition of multiple processes at low temperatures; a similar performance loss is observed when performances reached steady state. The restored performance from the reversible and the irreversible degradations highly depends on temperature. At low temperature, the performance recovery is only negligible with neat air operation (self-recovery), while full recovery is observed after cyclic voltammetry (CV) scanning. As temperature increased, so did the self-recovery performance. However, the total recovery performance decreased. Electrochemical impedance spectroscopy analysis indicates that the potential-dependent poisoning process was delayed at low temperature, and the removal of the sulfur species from Pt/C was inhibited during the self-recovery. Water balance analysis implies that the delay could be attributed to the effect of liquid water scavenging and the mass transport of SO_2 in the membrane electrode assemblies. The CV analysis confirms that the decomposition/desorption of the sulfur adsorbates was inhibited and indicates that the SO_2 crossover from the cathode to the anode side was also mitigated at low temperature.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have been considered one of the most promising clean energy technologies and suitable primary power sources [1]. Traces of impurities are known to exist in air, such as NO_x, SO_2, and organics. These impurities primarily originate from vehicle exhausts and industrial emissions, which can be introduced into the PEMFC cathode with air feeding streams. They can cause performance degradation and sometimes permanent damage to the membrane electrode assemblies (MEAs) [2–6]. To date, most of the cathode contamination studies focused on the effect of SO_2 on the degradation and recovery of PEMFC performance [6–18]. Severe degradation and a small partial slow self-recovery have been observed, and this finding is commonly accepted. The sulfur compounds adsorbed on the Pt surface tended to be oxidized to sulfate by CV scanning beginning at 0.9 V after they were reduced to adsorbed sulfur [10,16].

In our previous work, SO_2 contamination in PEMFC cathodes was observed to cause a multi-processes poisoning during constant current operation at 80 °C. The multiple poisoning processes result from: i) an irreversible adsorption of SO_2, which is independent of SO_2 concentration but depends on the coverage of the sulfur oxides; ii) a reversible adsorption of SO_2, which depended on the SO_2 concentration and the cathode potential; and iii) an anode

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* Corresponding author. Tel.: +1 8085931714; fax: +1 8085931719.
E-mail address: yunfeng@hawaii.edu (Y. Zhai).

[1] Currently at National Renewable Energy Laboratory, Golden, CO 80401, USA.

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http://dx.doi.org/10.1016/j.jpowsour.2013.08.054

poisoning by SO_2 crossover through the MEA [15]. The performance loss caused by the reversible process could be recovered by neat air operation. However, the loss caused by the irreversible process could only partially be recovered by CV scanning at high potentials after the sulfur adsorbate was reduced to sulfur on Pt/C. The electrochemical impedance spectroscopy (EIS) analysis indicated that the reversible adsorption of SO_2 also assists the oxygen reduction reaction (ORR) processes shifting from a direct four-electron to a series two-electron pathway [18].

The SO_2 adsorption on Pt or Pt/C has been extensively studied by physical/chemical characterizations and theoretical methods [19–35]. The effect of SO_2 adsorption on the ORR was also studied by ex-situ CV and/or the rotating ring disk electrode method [36,37]. These works indicated that SO_2 can dissociate to sulfur and sulfur oxides on Pt/C [19,20] or can be reduced catalytically or electrochemically to sulfur in the absence of oxygen [21]. Pre-adsorbed sulfur on Pt would significantly block oxygen adsorption [22]. Other studies concluded that the adsorbed SO_2 can be catalytically oxidized into SO_3 or SO_4 by pre-adsorbed oxygen [22–28]. The adsorbed SO_3 or SO_4 on different Pt crystal structures can also dissociate into adsorbed SO_2 and O at different temperatures [22,29]. These works provided important initial insights to understand the mechanism of SO_2 contamination in PEMFCs under certain operating conditions. Furthermore, these results indicate that the oxidation–reduction reactions of SO_2 on the Pt surface are complicated and depend on the historic conditions and the reaction environment, such as the temperature [30], adsorbate coverage [26,29], potential of the Pt electrode [31,32] and absorption of oxygen on Pt [22–24]. These findings suggested that the SO_2 contamination in PEMFCs is a complicated process that strongly depends on the operating conditions.

As a candidate power source for practical applications, PEMFCs are operated at varying operating conditions. It is difficult to predict the impact of SO_2 on the PEMFC's performance before understanding the SO_2 contamination mechanism at realistic operating conditions. Furthermore, the impurity's access to the catalyst and the removal of the product rely on the diffusion through the GDL and catalyst layer in the cathode. The change in water content and the variation of water management at different operating conditions will play an important role. Therefore, the influence of operating conditions on SO_2 contamination in PEMFCs needs to be elucidated by experimental investigation.

In this work, SO_2 contamination experiments were performed in PEMFCs with 2 ppm SO_2 at different cell temperatures. SO_2 exposure was followed by recovery via neat air operation (self-recovery) and subsequent CV scanning (CV recovery). The PEMFCs were then re-exposed to SO_2 to determine the effectiveness of the recovery and gain insights into the re-poisoning processes. EIS analysis was used to determine the influence of the operating conditions on the SO_2 contamination in PEMFCs. Two factors should be taken into account when studying the effect of cell operating temperature: (i) the SO_2 adsorption, which directly impacts ORR; and (ii) the SO_2 mass transport, which directs how the contaminant reaches the catalyst and involves the diffusion of SO_2 through the air and water vapor in the gas diffusion layer (GDL), followed by the liquid water and Nafion film in catalyst layer (CL).

2. Experimental

Experiments were performed using an evaluation system, single cells and testing processes that have been previously described [15,18]. FCATS™ G050 series test stations (Green Light Power Technologies Inc.) were used with 50 cm^2 single-cell hardware. The anode flow-field had a double channel serpentine configuration, while the cathode flow-field had a triple channel serpentine configuration. The MEA consisted of commercially available MEAs from Ion-Power Inc. with 0.4 mg Pt cm^{-2} loading and 50% Pt/C catalysts (KPTON® frame 50 cm^2, KPT-50, Lot#: 756). The cells were assembled with SIGRACET® SGL 25 BC gas diffusion layers (GDL) from SGL Technologies and PTFE gaskets on both the anode and cathode electrodes. The anode was fed with fully humidified (100% relative humidity, RH) H_2 and the cathode with 50% RH air; both the anode and cathode gas flow rates were maintained at a 2-fold stoichiometric ratio, current density of 0.6 A cm^{-2} and outlet back pressure of 48.3/48.3 kPa. A series of SO_2 contamination experiments were performed at cell temperatures of 45 °C, 60 °C, and 80 °C. A contaminant gas was injected into the humidified feed stream of the cathode to expose the PEMFC to SO_2. During this process, the humidification in the inlet gas was kept constant by increasing the temperature setting of the humidifier unit. The contaminant gas consisted of 93 ppm SO_2 in air (certified plus grade, Matheson Tri-Gas Inc.).

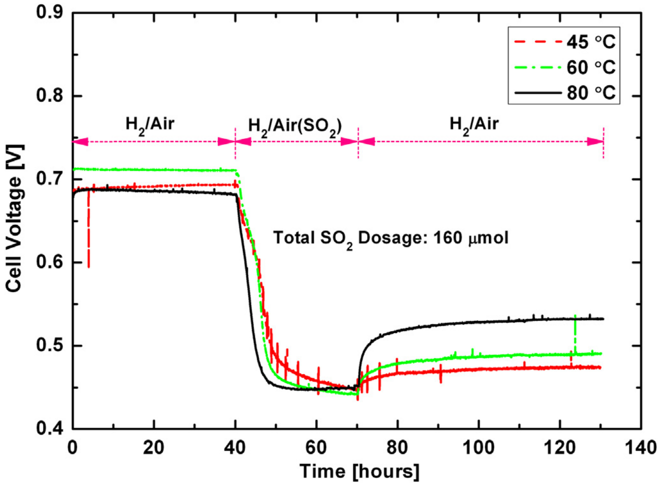

Fig. 1. Cell voltage changes with time during the 2 ppm SO_2 contamination experiments at different temperatures.

For the constant current operation (CCO) contamination experiment, PEMFCs were pre-poisoned for 40 h under neat H_2/air operation, followed by 30 h of 2 ppm SO_2 exposure and 60 h of self-induced performance recovery with neat H_2/air. All cells were operated at a current density of 0.6 A cm^{-2} during CCO. CV scanning was performed by switching to the H_2/N_2 operating mode with a Parstat 2273 from EG&G Instruments Corporation after cell activation and after CCO. Cell polarization curves were obtained before pre-poisoning and after CV recovery with neat H_2/air at the same operating conditions as those employed during CCO. During the polarization curves test, the cell was hold at the each set current density for 15 min (except 3 min for OCV). The cell voltage was recorded with an acquisition frequency of 1 Hz. Each MEA was again exposed to SO_2 for 20 h with operating parameters those used during the first exposure after a second pre-poisoning while operating with neat H_2/air for 20 h.

The CV scanning was conducted at 35 °C with fully humidified hydrogen or nitrogen in each side at a flow rate of 0.466 L min^{-1}. The hydrogen and nitrogen were supplied to the reference and working electrodes, respectively. A total of 16 scans were performed with a scan rate of 20 mV s^{-1}. The potential range of the first 13 cycles was 0.08–1.2 V vs. the hydrogen reference electrode (HRE), while that of cycles 14 to 16 was 0.08–1.5 V vs. HRE.

During the SO_2 contamination experiments, EISs from 10 kHz to 0.1 Hz (10 points per dec) were obtained with the ZPlot® (Scribner Associates) software with a Solartron SI1260 Impedance/Gain-