

Short communication

Activation of proton-exchange membrane fuel cells via CO oxidative stripping

Zhiqiang Xu¹, Zhigang Qi^{*}, Arthur Kaufman²

Plug Power Inc., 968 Albany Shaker Road, Latham, NY 12110, USA

Received 9 February 2005; received in revised form 24 February 2005; accepted 25 February 2005
Available online 20 July 2005

Abstract

It was found that CO oxidative stripping could enhance the performance of a proton-exchange membrane fuel cell. The procedure was performed by first allowing CO to adsorb onto the catalyst surface, and then potential scanning was carried out to oxidize the adsorbed CO. The evolution of CO₂ from CO oxidation increased the electrode active surface area, and this was one of the reasons leading to an enhanced fuel cell performance. The fuel cell achieved its maximum performance after several CO adsorption/CO₂ desorption cycles.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Activation; Incubation; CO; Fuel cells

1. Introduction

The use of carbon-supported catalysts and an ionomer such as Nafion within a catalyst layer has dramatically decreased Pt loading needed by a proton-exchange membrane (PEM) fuel cell [1–11]. The catalyst nanoparticles supported on carbon can have a surface area higher than 100 m² g⁻¹, while the presence of Nafion enables the entire catalyst layer to be active.

The low operating temperature and a quick start up distinguish a PEM fuel cell from other types of fuel cells. Such characteristics make PEM fuel cells very suitable power sources for portable electronics and for backing-up telecommunication systems.

A PEM fuel cell operated under ambient conditions normally needs quite a longer break-in period. During this break-in or preconditioning period, the performance of the fuel cell increases gradually; and finally, it reaches a plateau without

further increase in performance. To this point, the break-in procedure is thought to be complete.

We recently discovered that the performance of a PEM fuel cell could be further increased after the completion of a traditional break-in process by performing some novel activation procedures [12–16]. The first procedure includes evolving hydrogen via the reduction of protons at an electrode that is intended for activation [12,13]. The second procedure includes operating a fuel cell at elevated temperature and pressure first before running the fuel cell at ambient conditions [14–16]. Both procedures are very effective in activating and quickly incubating either hydrogen/air or methanol/air fuel cells.

In this paper, we report a new activation procedure that involves carbon monoxide (CO). Due to its notoriously strong adsorption onto catalysts, CO can seriously poison a PEM fuel cell; hence, it has been considered as a nuisance and obstacle to the development of fuel cells. Interestingly, we found that CO could be used to do some good things to PEM fuel cells.

2. Experimental

A catalyst mixture containing 30% Nafion and 70% E-TEK 20% Pt/Vulcan XC-72 was thoroughly stirred and

* Corresponding author. Tel.: +1 518 782 7700x1229;
fax: +1 518 782 7914.

E-mail address: zhigang_qi@plugpower.com (Z. Qi).

¹ Present address: SKC Power Tech., 850 Clark Drive, Mt. Olive, NJ 07828, USA.

² Present address: 69 Burnett Terrace, West Orange, NJ 07052, USA.

sonicated. It was then applied onto ELAT gas diffusion medium. The electrode was left in air to dry, followed by a further drying in an oven at 135 °C for 30 min. By the weight difference between the bare ELAT and catalyzed ELAT, the Pt loading was calculated to be 0.17 mg cm⁻². This electrode was then hot-bonded onto a Nafion 112 membrane with another electrode having a Pt loading higher than 1.0 mg cm⁻² at 130 °C for 3 min. The high Pt loading electrode was used as the anode during the following tests. Its high Pt loading made it certain that the anode was not limiting the performance of the MEA, as our purpose was to evaluate the lower Pt loading cathode.

Single fuel cell tests were performed using a homemade 10 cm² active area test fixture. The test fixture was composed of a pair of metal plates with serpentine flow-fields. The plates were coated with metal nitride for corrosion protection. Rod-like heaters were inserted into the plates to control the cell temperature. During the fuel cell operation, the load was varied using a rheostat.

Air and pure hydrogen were used as the reactants. They were passed through stainless steel water bottles prior to entering the cell to achieve a 100% relative humidity. The cell temperature, hydrogen humidification temperature, air humidification temperature, hydrogen back pressure, and air back pressure are denoted hereinafter as $T_{\text{cell}}/T_{\text{H}_2}/T_{\text{air}}$, $P_{\text{H}_2}/P_{\text{air}}$. For example, a condition with a cell temperature of 75 °C, hydrogen humidification temperature of 95 °C, air humidification temperature of 90 °C, hydrogen back pressure of 20 psig, and air back pressure of 30 psig, is expressed as 75/95/90 °C, 20/30 psig. The flow rates of air and hydrogen were controlled using flow meters to about 10 times stoichiometric for a current density of 2.0 A cm⁻².

Cyclic voltammetry of CO oxidation was carried out using a Solartron SI 1280B electrochemical measurement unit. During the CO adsorption process, a mixed gas containing 0.5% CO was used at the cathode side, and the cathode voltage was set at 0.50 V. Potential scanning was carried out between 0.5 and 1.0 V at a scan rate of 30 mV s⁻¹ in the presence of nitrogen. The main purpose of controlling the cathode voltage at 0.5 V or higher during both CO adsorption and potential scanning steps was to avoid hydrogen evolution because hydrogen evolution can also activate fuel cells [12,13], which would complicate our current study.

3. Results and discussion

Curve 1 in Fig. 1 shows the performance of an MEA after the completion of a conventional break-in procedure using pure hydrogen and air as the reactants. The test was carried out at 35/45/45 °C for more than 4 h. During this period, the fuel cell was set at around 0.4 V for most of the time; and periodically the cell voltage was scanned from open circuit to nearly 0 V. Every 30 min a $V-I$ curve was taken. It was observed that the fuel cell performance increased gradually, but after about 3 h no apparent further increase was observed.

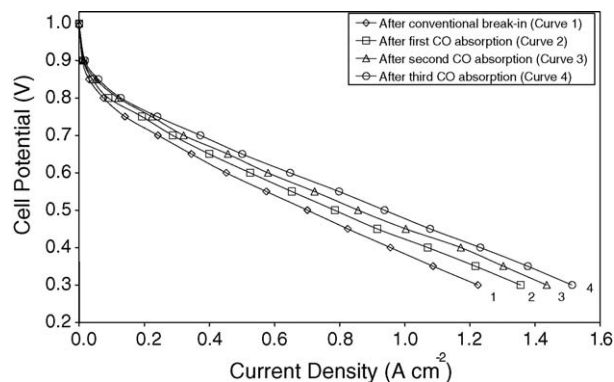


Fig. 1. Performance under conventional break-in and CO oxidative stripping conditions, respectively. Temperatures 35/45/45 °C; cathode Pt loading 0.17 mg cm⁻²; ELAT gas diffusion medium; Nafion 112 membrane.

The maximum performance that was achieved by performing a traditional break-in procedure is shown as curve 1 in Fig. 1.

The cell was then switched to open circuit, and air was replaced by nitrogen to pass through the cathode side. After about 30 min the nitrogen gas was replaced by a mixed gas containing 0.5% CO (balanced by 99.5% nitrogen), and the cathode of the cell was set at 0.5 V. Since CO can strongly adsorb onto the catalyst, the cathode should be quickly poisoned. The adsorption was allowed to last for about 30 min to ensure a full coverage of CO on the cathode Pt catalyst. A much shorter adsorption time could be enough, especially if a higher CO concentration were used. Then, the mixed gas was replaced by nitrogen to flush all the CO molecules that did not adsorb onto the catalyst out of the cathode compartment. Afterwards, the cathode potential was scanned from 0.5 to 1.0 V for three times. A sharp CO oxidative stripping peak at ca. 0.76 V was observed during the first cathodic scan, and no peaks were observed during the second and third scans. Obviously, CO was oxidized to CO₂ during the first scan, and the resulting CO₂ was stripped off the catalyst surface. Curve 5 in Fig. 2 shows the cyclic voltammogram during the first scan.

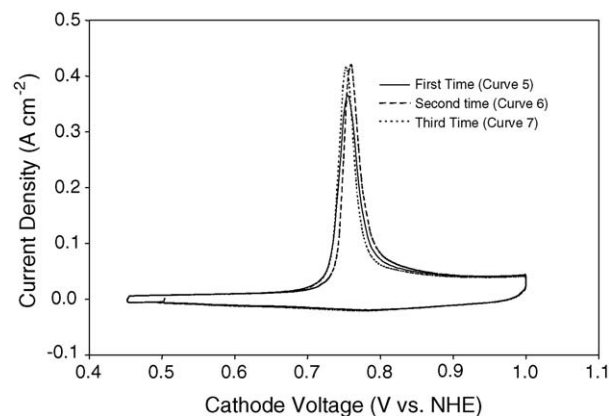


Fig. 2. Cyclic voltammograms obtained from CO oxidative stripping during the first potential scan. Potential scan rate 30 mV s⁻¹; other conditions were the same as in Fig. 1.

After the above CO oxidative stripping experiment, air was conducted into the cathode compartment, and a second $V-I$ curve was taken. The result is shown as curve 2 in Fig. 1. Very interestingly, curve 2 is apparently higher than curve 1 in the entire current density region. This means that a CO adsorption/ CO_2 desorption process pushed the fuel cell performance over the limitation capped by a traditional break-in procedure.

When another CO adsorption/ CO_2 desorption was performed according to the same procedure, the CO oxidation peak (curve 6, Fig. 2) was about 5% larger than the first one (curve 5, Fig. 2). This indicates that the first CO adsorption/ CO_2 desorption process increased the catalyst surface area available for CO adsorption and thus for fuel cell reactions. When the fuel cell performance was measured after this second CO adsorption/ CO_2 desorption process, a further increase was observed, as shown by curve 3 in Fig. 1, indicating that a further activation occurred due to the second CO adsorption/ CO_2 desorption process.

A CO adsorption/ CO_2 desorption was performed for the third time. Curve 7 in Fig. 2 shows the CO oxidative stripping cyclic voltammogram during the first potential scan. The peak height was similar to that of the second peak (curve 6), implying that the third CO adsorption/ CO_2 desorption did not further increase catalyst surface area for CO adsorption. However, when the cell was tested in the fuel cell mode, another increase was observed, as shown by curve 4 in Fig. 1.

A fourth CO adsorption/ CO_2 desorption process was also performed, and a cyclic voltammogram similar to curves 6 and 7 was obtained. When the fuel cell was tested in the fuel cell mode again, no further increase in performance was observed. So, the maximum activation effect had been achieved after the first three CO adsorption/ CO_2 desorption cycles.

We reported another method to activate a low temperature PEM fuel cell by operating it at elevated temperature and pressure first [14–16]. In order to see how much activation had been achieved by the four CO adsorption/ CO_2 desorption cycles, another new MEA with the same composition was activated by operation at 75/95/90 °C and 20/30 psig for 2 h. Then, the condition was returned to 35/45/45 °C, and the performance was measured. Table 1 summarizes the maximum performance at a fuel cell voltage of 0.4 V achieved by the conventional break-in, CO adsorption/ CO_2 desorption, and elevated temperature and pressure methods, respectively. It can be seen that CO adsorption/ CO_2 desorption achieved ca. 29% higher maximum performance

than a traditional break-in method, and that activation using elevated temperature and pressure achieved ca. 9% higher maximum performance than CO adsorption/ CO_2 desorption method.

Although activation by CO adsorption/ CO_2 desorption is less effective than activation using elevated temperature and pressure, it has its own advantages. For example, when operation under elevated temperature and pressure could not be easily performed, activation by CO adsorption/ CO_2 desorption could still achieve most of the enhanced portion of performance.

4. Conclusions

A new activation method using CO adsorption/ CO_2 desorption was reported. This method can be performed at ambient conditions without increasing cell temperature and reactant backpressure. Three CO adsorption/ CO_2 desorption cycles were needed to achieve the maximum performance under our experimental conditions. This maximum performance was about 29% higher than that obtained by a traditional break-in procedure, but was slightly lower (ca. 9%) than that achieved by a high temperature and pressure activation method.

Acknowledgements

The authors are grateful to Dr. John Elter, Mr. Daniel Beaty, and Ms. Cynthia Mahoney White of Plug Power for their review of this article and for their permission to publish the results.

References

- [1] H.G. Petrow, R.J. Allen, U.S. Patent No. 4,166,143 (1979).
- [2] I.D. Raistrick, U.S. Patent No. 4,876,115 (1989).
- [3] H.G. Petrow, R.J. Allen, U.S. Patent Re. 33,149 (1990).
- [4] M.S. Wilson, U.S. Patent No. 5,211,984 (1993).
- [5] Y. Fukuoka, M. Uchida, N. Eda, U.S. Patent No. 5,723,173 (1998).
- [6] M. Watanabe, K. Sakairi, U.S. Patent No. 5,728,485 (1998).
- [7] E.A. Ticianelli, C.R. Derouin, A. Redondo, S. Srinivasan, J. Electrochem. Soc. 135 (1988) 2209.
- [8] Z. Poltarzewski, P. Staiti, V. Alderucci, W. Wieczorek, N. Giordano, J. Electrochem. Soc. 139 (1992) 761.
- [9] M.S. Wilson, S. Gottesfeld, J. Electrochem. Soc. 139 (1992) 28.
- [10] M.S. Wilson, S. Gottesfeld, J. Appl. Electrochem. 22 (1992) 1.
- [11] M. Uchida, Y. Aoyama, N. Eda, A. Ohta, J. Electrochem. Soc. 142 (1995) 463.
- [12] C. He, Z. Qi, M. Hollett, A. Kaufman, Electrochem. Solid-State Lett. 5 (2002) 181.
- [13] C. He, Z. Qi, A. Kaufman, U.S. Patent No. 6,730,424 (2004).
- [14] Z. Qi, A. Kaufman, J. Power Sources 111 (2002) 181.
- [15] Z. Qi, A. Kaufman, J. Power Sources 114 (2003) 21.
- [16] Z. Qi, A. Kaufman, U.S. Patent No. 6,805,983 (2004).

Table 1
Maximum performance achieved by traditional break-in, CO adsorption/ CO_2 desorption, and elevated temperature and pressure methods

Current density at 0.40 V (A cm^{-2})				
Break-in	1st CO/ CO_2	2nd CO/ CO_2	3rd CO/ CO_2	Elevated T/P
0.956	1.071	1.172	1.232	1.342