Investigation Of Cell Operation Conditions For Co Tolerance Improvement of PEMFC

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ABSTRACT

The investigation is to experimentally study the transient CO poisoning test with different cell operation conditions. One is fixing the cell voltage and the other is fixing the current density. In the former condition, the voltages are fixed at 0.5, 0.6, 0.7V, respectively, whereas the current densities are fixed at 600, 1000, 1200mA/cm²; respectively, in the latter one. In the transient poisoning test, the cell performance will be declined with time. The poisoned polarization curves are determined as soon as the performance subjected to CO poisoning reaches a steady state. Then, it will determine which one has a better performance in CO poisoning test and find out the difference between these two methods. With fixed cell voltage to perform transient CO poisoning test, it indicates that changing cell voltage cannot transform the stable poisoned polarization behaviors, whereas with fixed current density, it can get a better recovery performance at a fixed CO concentration (52.7ppm).

INTRODUCTION

The Proton Exchange Membrane Fuel Cell (PEMFC) uses hydrogen and oxygen as the fuel. But storing

CO is adsorbed directly onto either bare Pt sites or Pt-H sites to reduce the number of available catalytic sites. This is so-called CO poisoning.

Numerous theoretical and experimental investigations have addressed the improvement of PEMFC CO tolerance. Several investigators have suggested techniques to reduce the effect of CO poisoning. These include increasing the ability to catalyze the oxidation of CO; weakening the adsorption of CO by these catalysts; adding an oxidant into the anode fuel stream to oxidize CO; to increasing the anode potential to oxidize CO, and changing the thermodynamic conditions.

The first solution is to use alloyed catalysts. This method is to add second or third metal to the Pt catalyst to form a new alloy to improve CO tolerance. Pt-Ru alloy is the alloy most commonly used as a PEMFC catalyst in commercial fuel cells, because the Pt-Ru catalyst increases CO tolerance (Wasmus, 1999). Some studies have elucidated the mechanism of the CO reaction on the Pt-Ru catalyst (Zhang, 2004).

Watanabe and Motoo (1975) used the Ru surface to form Ru-OH to oxidize CO, which is adsorbed on the catalyst to form CO₂. CO is removed from the surface of the catalyst, whose reaction area thus increases, improving cell performance. Ru can promote the oxidation of CO, and so Pt-Ru catalyst improves CO tolerance.

CO tolerance can also be improved by feeding oxidant into the anode. Increasing the CO concentration increases the rate of recovery of cell performance over that associated with alloy catalysts. If the CO concentration is increased, an additional procedure must be performed to bleed an oxidant into the anode fuel stream to oxidize CO. The bleeding oxidant can be air, oxygen and hydrogen peroxide. Some investigations have studied bleeding oxidant.

Christoffersen et al. (2001) used “density functional theory” to calculate every kind of dual metal catalyst surface characteristics and the corresponding CO adsorptive power. They concluded that CO is adsorbed by Ru of Pt-Ru to the catalyst surface, and, then, the adsorbability of CO on Pt decreases. Therefore, Ru can reduce CO poison effect.
Watanabe et al. (1999) applied a theoretical calculation for Pt-Ru catalyst adsorptive power with CO. Their results supported the conclusion of Christoffersen et al. (2001). Therefore, they indicated that there are two ways to increase CO tolerance by Pt-Ru. One is that Ru-OH can oxidantize CO, the other is that Ru can reduce the CO adsorption of Pt. These two effects exist simultaneously. Gastiger et al. (1994) considered that the optimum ratio between Pt and Ru to increase CO tolerance is 1:1.

Gottesfeld and Pafford (1988) took a new approach to solve the problem of poisoning in PEMFC. They attempted to generate an oxidative surface environment at the anode Pt catalyst, so CO was removed by oxidation to form CO$_2$. The oxidation of CO by oxygen at the Pt catalyst can proceed only at a temperature of over 100 ºC and a PEMFC operation temperature of approximately 80 ºC. However, injecting oxygen into the impure anode fuel stream improved cell performance. Therefore, this new approach effectively improves CO tolerance. At a CO concentration of 100ppm, injection 2-5% oxygen could completely restored cell performance. The reaction is shown as follows (Gilman, 1964):

$$ \text{O}_2 + 2\text{Pt} \rightarrow 2\text{O}_{\text{ads}} $$

$$ \text{CO}_{\text{ads}} + \text{O}_{\text{ads}} \rightarrow \text{CO}_2 + 2\text{Pt} $$

Murthy et al. (2001) used commercial MEA to perform a CO test. In a steady-state test, injecting 5% air almost completely recovered the performance of the PEMFC at 500ppm CO. With 3000ppm CO, complete recovery was not achieved, even when 15% of the air was bled. In the transient measurement, CO concentration in all instances changed with time. They considered that air bleeding could reduce the rate of CO poisoning and considerably recover the cell performance.

Murthy et al. (2003) also studied thermodynamic effect on CO tolerance. They still used the same commercial MEA to change cell temperature and backpressure. Raising the cell temperature from 70 to 90 ºC would increase CO tolerance that it is due to a temperature dependence of the adsorption. Increasing backpressure from 101kPa to 202kPa might have an increase in the permeability for oxygen. When oxygen arriving to the anode side would oxidize CO and improve cell performance. In the transient measurements, they found that poisoning rates were substantially four times lower with an increase in pressure and fourteen times with an increase in temperature.

Uribe et al. (2004) used a simple anode modification to improve CO tolerance for proton exchange membrane fuel cell. The modification was to reconfigure anode by placing a composite film containing inexpensive materials onto the gas diffusion layer. These materials can catalyze the oxidation of CO with O$_2$ to form CO$_2$ at 80 ºC. The source of oxygen is from a small amount of air injected along with hydrogen into the anode.

Murthy et al. (2004) announced a new development of a stationary MEA, which prove a low decay rate of cell performance when fuel is reformated with CO. Using some air-bleed to mitigate CO poisoning effects.

The investigation is to define suitable CO poisoning test condition for PEMFC. First, the test samples of fuel cell are fixed at two specific conditions to perform the transient CO poisoning experiments. One is to fix the voltage, the other is to fix the current density. In the former condition, the voltages are fixed at 0.5, 0.6, 0.7V, respectively, whereas the current densities are fixed at 600, 1000, 1200mA/cm$^2$, respectively, in the latter one. In these tests, the anode is fed by pure hydrogen in the first 5min., then, it is changed to H$_2$/CO, where the CO concentration is specified as 52.7ppm. The cell performance will be varied with time. The poisoned polarization curves are determined as soon as the performance subjected to CO poisoning reaches a steady state. Then, it will determine which one (cell voltage or current density) has a better performance in CO poisoning test and find out the difference between these two methods.

**EXPERIMENTAL**

This fuel cell test station consists of four components, which are the electronic load, MFC readout power supply, power supply, gas pipelines controller. Utilizing this system can change operation conditions, like temperature, humidification, flow rate, pressure, cell potential, etc, required by PEMFC performance evaluation. The elements of test station are described as follows.

The electronic load uses the style of HP6060b. It measures current range between 0 and 60A. The maximum power output that load box can support is 300watts. Electronic load can measure cell voltage and be used to control cell voltage and current. Eventually, it will consume cell power production in the test.

The PC-540 MFC Readout Power Supply can display and control units for precision gas control in conjunction with MFCs. This apparatus has multiple channel instrumentation that it can completely control up to four MFCs at the same time. In the present experiment, the flow rate controller will control three flow meters, which include anode gas, cathode gas and additional gas meter. These gas meters are anode (H$_2$), cathode (O$_2$) and bleeding (air), respectively.

This apparatus is a power source switch that
The PEMFC has six major components— the membrane electrode assembly (MEA), the gas diffusion layer (GDL), the gasket, the gas flow channel and the current collector. The PRIMEA series 5561 MEA is a commercial product from Gore. The membrane in the middle has a thickness of 35um and the catalyst loads are of 0.45mg/cm² Pt-Ru alloy (1:1) on the anode and 0.6mg/cm² Pt on the cathode. The active area of the membrane is 25cm² and the border area is 100cm². The gas-diffusion layers used are CARBEL CL GDL with a thickness of 0.4mm. A double channel serpentine flow-fields (with channel and rib widths of 0.1cm each and a channel depth of 0.1cm) is used on both the anode and cathode sites. The anode and cathode flows are co-current. The current collector consists of gold-plated copper. The current collector board conducts electric current from the cell. Eight lubricated bolts are inserted into tapped holes on one of the end plates, and the cell is compressed with a torque of 120kgf cm. The experimental conditions for these tests are fixed. The fuel flow rates of the anode and the cathode are determined from the theoretical volume flow rate, which can generate 1A. They are 7.6 and 3.8cc/min/A for hydrogen and oxygen, respectively. Then, for the anode, the rate is multiplied by the stoichiometric ratio 1.37 to yield a value of 10.4cc/min/A, whereas for the cathode, the rate is multiplied by 1.84 to yield 7cc/min/A. The cathode stoichiometry exceeds that of the anode because the oxygen is less reactive. The exit pressures of the anode and cathode sides are 101kPa. The cell temperature is held at 65°C and the corresponding temperatures of the anode and cathode humidifiers are held at 80°C and 70°C, respectively. These temperatures make the fuel sufficiently humid to cross through the membrane and optimize the cell performance with a cell temperature of 65°C. Table 1 summarizes the operation conditions of fuel cell in this work.

| Table 1. Fuel cell operation conditions. |
|-----------------|-----------------|
| Cell temperature | 65°C            |
| Humidification  | Anode: 80°C, Cathode: 70°C |
| temperature     |                  |
| Backpressure     | Anode, Cathode: 1atm |
| Fuel flow rates  | H₂: 10.4cc/min/Amps O₂: 7cc/min/Amps |
| Min. fuel flow rates | H₂: 104cc/min O₂: 70cc/min |
| Stoichiometry    | H₂: 1.37, O₂: 1.84 |
| Feed stream      | Anode: H₂, H₂+ CO Cathode: O₂ |
| Transient conditions: | Fix cell voltage: 0.5, 0.6 and 0.7V Fix current density: 600, 1000 and 1200mA/cm² |
| CO concentration | 52.7ppm |

RESULTS AND DISCUSSION

Poisoning Effects of Fixed Cell Voltage

The results of transient experiments, whose cell potentials are fixed at 0.5, 0.6, and 0.7V are shown in the Figure 1. In general, it can be found when fuel is changed to H₂/CO, the cell performance of resultant current density decays very quickly. It is because that fuel cell operation temperature is always maintained between 65°C and 85°C, in this range, CO has a stronger adsorbability with Pt catalyst than that of H₂. In other words, it will take over the active site of catalyst when CO presents in reaction chamber. Therefore, the less active site of catalyst is available for the hydrogen reaction that reduces the cell performance.

In Fig. 1, the current density declines from 735mA/cm² (pure H₂) to a stable poisoned current density 370mA/cm² after 65min. in the case of 0.7V. As the cell voltage fixes at 0.6V, the current density decreases from 1460mA/cm² (pure H₂) to 530mA/cm² after 40min. For 0.5V case, it declines from 2200mA/cm² to 700mA/cm² after 35min. From these observations, it is found that the performance decline rate becomes faster at the lower fixed cell voltage. The reason is that the lower cell voltage produces a higher current density, which requires higher fuel flow rate. Consequently, it results in a higher supply amount of CO, consequently, the accumulation and adsorbed rate of CO becomes
higher in the reaction chamber. Finally, the competition of adsorbed reaction with Pt alloy catalyst between hydrogen and CO reaches to a balance state, defined as the steady state. The corresponding times for each fixed voltage to reach steady state are mentioned above.

When the steady state is reached, the anode fuel is turned back to pure hydrogen and no CO exists in the fuel stream at all. Under this circumstance, the CO must be desorbed from catalyst surface by pure hydrogen or oxidized by the anode catalyst alloy. The recovery of cell performance almost simultaneously takes place as the fuel is turned back to pure hydrogen as shown in Fig. 1. However, it can only recover to about 80 percentage of the original performance after 30min. of purging pure hydrogen, indicating that there is a lot of CO still adsorbed on the catalyst and cannot be removed completely.

Fig. 1. Transients poisoning and recovery performances with different poisoning conditions (0.5, 0.6 and 0.7V)

Figure 2 shows the baseline polarization curve, the poisoned and recovered polarization curves with different poisoning conditions (0.5, 0.6 and 0.7V). In this figure, it is significant to find that for a given concentration of CO (52.7ppm) the resultant steady state poisoning polarization curves are almost coincident no matter the applications of different fixed cell voltage in these transient tests, which the cell operations and fuel humid temperatures are the same. It implies that under a given CO concentration, the hydrogen and CO adsorption reactions to the Pt alloy catalyst have a fixed balance state, or a constant polarization behavior. The only difference is the duration to reach the steady state.

In Fig. 2, it also shows that the recovery rate after purging the pure hydrogen is faster for the case of lower cell voltage in the transient tests. The similar reason for poisoning effect has been given in the discussion of Fig. 1. The cell at the lower voltage gains a higher current density, which requires the higher fuel flow rate. The higher rate may accelerate CO desorption from catalyst. The other reason is that the fuel cell at low voltage can force CO to proceed oxidation reaction to remove itself from catalyst. Therefore, the transient experiment at a lower fixed voltage, such as 0.5V, can get a better recovered rate (more than 85%) in the Fig. 1. This explains why the different polarization behaviors show up in recovered performance with different transient poisoned conditions (0.5, 0.6 and 0.7V).

Poisoning Effects of Fixed current density

Next, the transient poisoning tests are performed at different fixed current densities. In Figure 3, it shows three cell voltages transient curves, which the corresponding fixed current density are 600, 1000 and 1200mA/cm², respectively. In this case, the cell performance, expressed as cell voltage, decays very fast when H₂/CO (52.7ppm) fuel stream is introduced into anode. It can cause a rise of anode potential, relatively; a decrease in cell potential because CO adsorption reduces the catalyst active site. Finally, the performance subjected to CO poisoning reaches to a steady state as shown in Fig. 3. The cell voltage for a fixed cell current density of 600mA/cm² decays from 0.725V to a stable voltage 0.53V when anode fuel contains 52.7ppm CO after 50min. The one fixes at 1000mA/cm², the voltage decays from 0.662 to 0.410V after 45min. and the one at 1200mA/cm² decays from 0.632 to 0.355V after 30min. It can find that the higher fixed current density can result in a
faster poisoned rate. The reason is same as that in Fig. 1.

Fig. 3 Transients poisoning and recovery performances with different poisoning conditions (600, 1000 and 1200mA cm\(^{-2}\)).

In Figure 4, it shows the baseline polarization curve, the poisoned and recovered polarization curves with different poisoning conditions (600, 1000 and 1200mA cm\(^{-2}\)). It can observe that a better CO poisoned tolerance performance can be obtained when cell is fixed at higher current density (1200mA/cm\(^2\)) to perform the transient test. In this situation, the CO poisoned phenomenon is indicated by the decrease of cell voltage. The CO poisoning effect always makes anode potential rising and causes overall cell performance to decline. However, CO on the catalyst surface can perform oxidative reaction if the anode potential rises to the CO onset potential of oxidation. In Fig. 3, it can calculate the rise of stable anode potential under 52.7ppm of CO in different current density conditions, such as 600, 1000 and 1200mA/cm\(^2\). They are 0.175, 0.252 and 0.277V, respectively. The higher anode overpotential cause more CO removed from catalyst surface and obtain a better CO tolerance. Therefore, the transient condition with 1200mA/cm\(^2\) has the best steady poisoned polarization performance as shown in Fig. 4. On the contrary, the transient poisoned condition of fixed cell voltage may limit the change of anode potential. Therefore, it cannot oxidize CO from catalyst surface in the stable poisoned state. The stable values of CO adsorption are the same for any transient conditions (0.5, 0.6 and 0.7V), and the steady poisoned polarization behaviors are almost coincident to each other.

Fig. 4 The baseline polarization curve, the poisoned and recovered polarization curve with different poisoning conditions (600, 1000 and 1200mA cm\(^{-2}\)).

In Figure 5, it shows the anode polarization curves obtained from the poisoned polarization curves in Figs. 2 and 4. At first, it should describe the polarization behaviors with pure hydrogen fuel; no CO poisoning. The typical polarization behavior, fed with pure hydrogen, for fuel cell is shown in the baseline curve of Fig. 2 and 4. There are three main effects that cause cell potential to drop. They are the kinetic losses, ohmic losses and mass transport limitations. The initial fall is associated with the poor electrode kinetics at a voltage close to the rest voltage. This sharply sudden drop is due to the sluggish kinetics of the oxygen reduction reaction. As the current density rises, the cell potential varies nearly linearly with current density. It is mainly due to ohmic and mass transport losses in solution between electrodes. The anode overpotential can be neglected when anode is fed with pure hydrogen. So, the cell potential drop in the typical polarization curve can be treated as the drop of cathode potential. The anode potential is calculated from the difference between the cell potential with pure hydrogen and the one with H\(_2\)/CO at the same current density. Then, the polarization curve is obtained from the collection of anode potentials for all of current densities. In Fig. 5, it can observe that the rising rate is smaller with a higher current density in the transient poisoning test. The higher fixed current density can force anode potential to rise to the value above onset one of CO oxidation and, then, to remove CO from catalyst surface. Therefore, it causes a better CO tolerance, which has a lower anode potential slope. On the other hand, in the transient condition of 600mA/cm\(^2\), its anode potential slope is higher than the others (1000, 1200mA/cm\(^2\)). It is because that the anode potential...
only rises to 0.175V in the stable poisoned state when the current density is fixed at 600mA/cm². This resultant potential is lower than the onset potential of CO oxidation, so it cannot improve CO tolerance.

Fig. 5 Anode potential due to CO (52.7ppm) poisoning with different transient poisoning conditions (0.5, 0.6 and 0.7V), (600, 1000 and 1200mA cm⁻²)

Uribe et al. (2004) found that, at a current density of 0.6A/cm², the losses to the application of 100ppm CO are no more than 40mV with 4% of air. But an injection of 4% air is not sufficient to restore 80% of the current density when the voltage is of 0.6V. The present study used the same commercial MEA as that used by Murthy et al. (2001) to perform a CO poison test. Their data showed that the transient performance at 0.6V (close to the present experiment with a current density 1200mA/cm²) of this MEA with air bleeding could reduce the CO poisoning rate and get a better recovery cell performance. The results obtained herein verify such conclusion as well.

In the transient test of fixed cell voltage, the discrepancy among the stable poisoned polarization curves with different poisoning conditions is insignificant. The anode polarization curves are more or less the same in this case. Its potential slope is higher than the one in fixed current density case (1000, 1200mA/cm²). It can conclude that changing cell current density to a higher value can get a better recovery performance, whereas it cannot change the stable poisoned polarization behaviors in the transient experiment of fixed cell voltage.

CONCLUSIONS

The objective of this work is to experimentally investigate the transient CO (52.7ppm) poisoning test with fixed cell voltage and current density conditions, respectively. When fixed cell voltage to perform transient CO poisoning test, the anode potential is restricted to change. Therefore, the CO adsorption rates at anode catalyst with any voltage conditions reaches to the same steady-state values. So, the poisoned polarization curves under different cell voltages to do CO poisoning tests are alike. For the CO poisoning tests with fixed current density, using higher current density can get a better recovery performance. The higher current density can promote the anode potential to achieve the onset potential of CO oxidation that causes CO removed from Pt surface. The steady adsorption rate of catalyst is decreased following the rise of current density condition in the transient tests. Apparently, it can improve the cell performance by using this method.

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