Experimental Investigations into Phosphoric Acid Adsorption on Platinum Catalysts in a High Temperature PEM Fuel Cell▲

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Abstract

Dynamic testing of a phosphoric acid-based high temperature PEM fuel cell shows a peculiar phenomenon. A certain current loss is observed after temperature cycling at constant voltage. This loss is incidentally recovered by applying a cell voltage spike to open circuit voltage. Experimental investigations into temperature, cell voltage, and ageing effects show that this phenomenon might occur due to the orientation of the adsorbed phosphate species on the platinum catalyst surface. Along with some supporting literature and experimental results, a hypothesis is presented in order to explain this occurrence. Phosphoric acid adsorption hysteresis on platinum catalyst due to temperature cycling could cause the temporary cell current loss. Electrode potential-dependent molecule symmetry of adsorbed phosphate ions could bring about the cell current recovery.

Keywords: Adsorbate Orientation, Fuel Cells, HT PEM, Hysteresis, Phosphoric Acid Adsorption, Platinum Catalysts, Temperature Cycling

1 Introduction

Automotive industries worldwide are introducing polymer electrolyte membrane (PEM) fuel cell driven cars into the market. The Nafion-based fuel cell, which operates at 80 °C, is currently the most suitable candidate for such an application. The reduction in system complexity nevertheless requires the fuel cell to operate at moderately higher temperatures (>120 °C) in order to be more tolerant to carbon monoxide poisoning [1–4] and less dependent on membrane humidification. The polybenzimidazole (PBI)/phosphoric acid-based high temperature (HT) PEM fuel cell is a promising alternative. It does not require membrane humidification and is much more tolerant toward catalyst poisoning at its higher operating temperatures (~160 °C) [5, 6].

The main drawback of the HT PEM fuel cell is the low power density at cell voltage of 0.6 V (<0.4 W cm^{-2}) compared to its low temperature counterpart (>0.8 W cm^{-2}). Both fuel cell types undergo hydrogen oxidation on the anode and oxygen reduction on the cathode. The limited efficiency of the HT PEM is attributed to the slower ORR kinetics [7]. Phosphoric acid electrolyte hinders the oxygen transport through the electrolyte on the cathode as well as adsorbs strongly on the catalyst surface, thereby, reducing the available active reaction area. Any further improvements in the cell's power density would, therefore, need a better understanding of the influence of phosphoric acid on the cell performance.

▲ *Paper presented at the 7th Symposium on Fuel Cell Modelling and Experimental Validation (MODVAL7), March 23rd–24th 2010, Morges (Lausanne), Switzerland.*

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2 Cell Current Hysteresis and Preliminary Studies

For automotive applications, the fuel cell candidate needs to be relatively stable under dynamic operations such as regular shut downs and start ups. This translates essentially into cooling the fuel cell from its high operating temperatures down to ambient temperature when it is shut down and then heating up again during started up. Thus, stability after temperature cycling is an important criterion for any fuel cell type for automotive application.

One such temperature cycling of the HT PEM test fuel cell is depicted in Figure 1. While holding the cell voltage at 0.6 V, the test cell is allowed to cool down from its operating temperature of 160–40 °C, and then heated up again to 160 °C. Consequent to the cooling, the cell current drops gradually until the temperature reaches 40 °C and increases as the temperature rises to 160 °C. Instead of reaching its previous value, the cell current rise ceases at a reduced value (approximately 90% of its previous value). The system is in a state of equilibrium and does not show any further increase in cell current. This loss in cell current is then incidentally recovered when the cell voltage is increased to open circuit voltage (OCV) for a short duration of 2–3 s and brought back to 0.6 V. The occurrence of such a phenomenon for a HT PEM fuel cell has never been reported in literature.

The presence of phosphoric acid in the electrodes, which distinguishes the HT PEM fuel cell from the Nafion-based fuel cell, provides a good starting point for investigations. The earliest study carried out by Habib and Bockris investigates phosphoric acid adsorption on platinum and gold catalysts through FTIR experiments. This work concludes that the phosphoric acid adsorbs on the platinum surface and that the adsorbate concentration is potential dependent, as shown here in Figure 2.

The surface concentration of the adsorbate (H_3PO_4) in relation to the electrode potential shows a definite peak at approximately 0.8 V. This observed behavior (the surface concentration seems to increase until this electrode potential value is reached and then drops right after) was reported to be partially associated with the water desorption. In a following publication, a comparative study of two different electrolytes, CF_3SO_3H and H_3PO_4, was carried out. Using similar FTIR experimental investigations, the adsorption of $CF_3SO_3^-$ and H_3PO_4 on platinum as a function of potential was compared (Figure 3a). In addition, an extrapolated estimation of adsorption as a function of temperature at constant voltage was presented using Bockris–Swinkels isotherm (Figure 3b).

It can be seen in Figure 3a that only the surface coverage of phosphoric acid on platinum increases from low potentials to intermediate potentials. After reaching a peak value, it begins to decrease as the electrode potential increases. In comparison, the $CF_3SO_3^-$ shows only a minimal response to the electrode potential. On the other hand, both electrolytes show a relatively similar adsorption behavior in response to temperature changes. Although
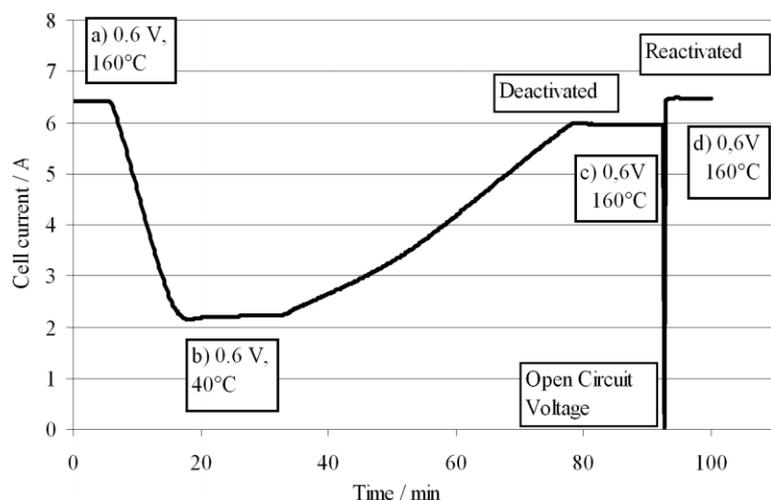
Fig. 1 Temperature cycling effect and cell current recovery.
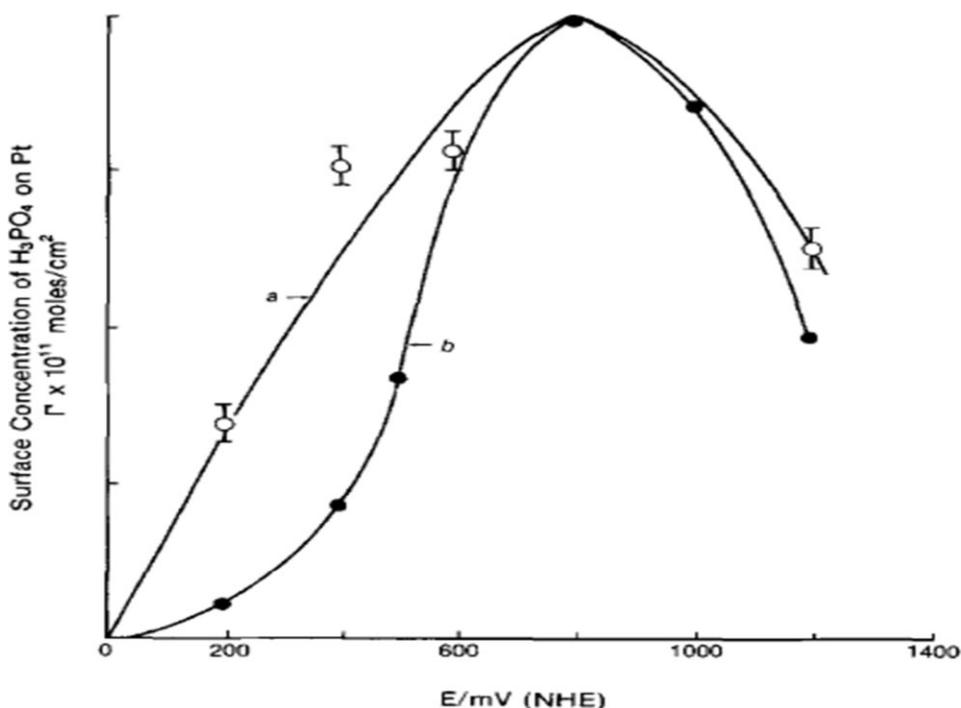
Fig. 2 Surface concentration Γ of H_3PO_4 on Pt as a function of potential. (a) Based on IR peaks and (b) based on radiotracer measurements. The scoring on the Y-axis is in units of 5 [8].
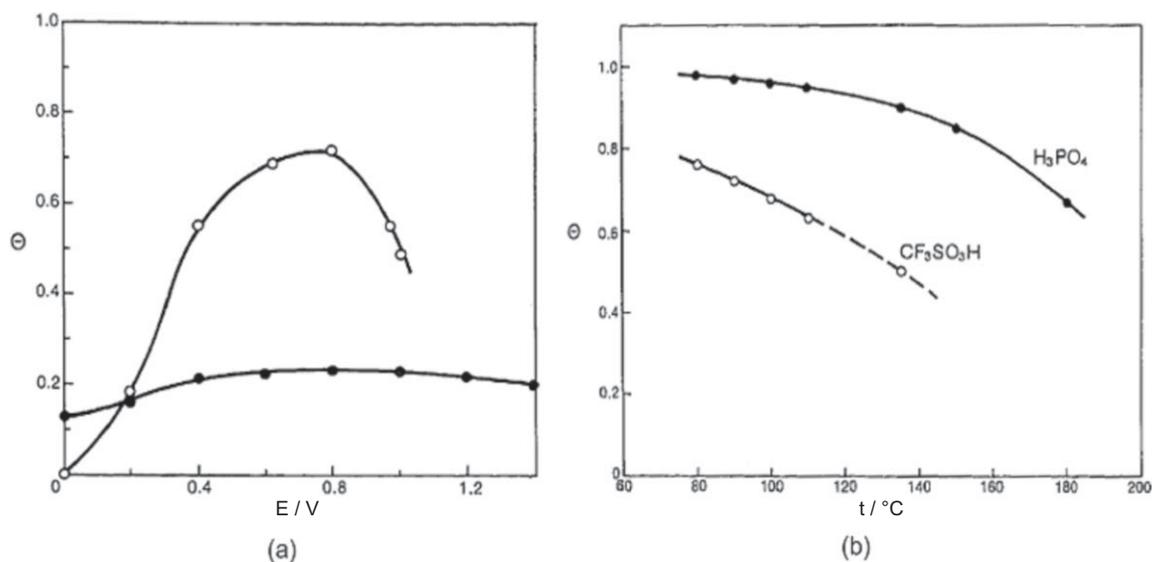
Fig. 3 Surface coverage on platinum (a) as a function of potential (H_3PO_4 ($\bigcirc$), $CF_3SO_3^-$ ($\bullet$)) and (b) as a function of temperature (extrapolated) [9].

the magnitudes vary, surface coverage in both cases increases with decreasing temperature. Both temperature and potential dependence of adsorbed phosphoric acid on platinum catalysts hints toward the cause of the reported phenomenon. Experimental investigations and discussions are presented in the following section followed by the formulation of the hypothesis.

3 Experimental Results and Discussion

3.1 Experimental Setup

The experimental setup consists of the single test cells mounted on fuel cell test benches C100 from FuelCon AG. The fuel cell hardware comprises of two metal alloy blocks that provide connections for fuel flow inlet and outlet, temperature, voltage sensor, and the current collector plate. The inner side of this hardware is the graphite plate with a square shaped flow field in the center with flow channels of serpentine design. The total area of the flow field is approximately 10 cm^2. The Pt/C electrode paste is prepared in-house, printed on the GDL material, and has a combined thickness of 300 μm. Both the anode and cathode are identically prepared with an estimated platinum loading of 1.5 mg cm^{-2}. A 10 cm^2 dry PBI membrane film (thickness of 30 μm) is doped with 85% phosphoric acid and has an impregnated thickness of around 50 μm. This membrane has a phosphoric acid loading of ca. 80 wt.% and is sandwiched between the electrodes.

For the structural integrity of the MEA, two additional components are used. A thin film of about 25 μm, made up of insulating Kapton material is used to hold the membrane in place. The MEA is then sealed between two polytetrafluroethylene (PTFE) gaskets. These gaskets are about 200 μm thick and provide electrical insulation as well as impermeability to reactant gases. The fuel cell hardware blocks with the MEA in between are screwed together to prevent any gas

leakages. The test cell is then mounted on the test bench, which provides operational support.

The C100 test bench has connections for gas supply, heating rods, temperature sensors, as well as the cell current and voltage sensors. The complete overview of the operational test cell parameters is observed and controlled from the software interface. Temperatures, pressures, gas flow rates, cell voltage, and cell current can be varied by manual inputs from this interface. It is also possible to run user-defined scripts for long-term trials. Along with hydrogen and air as reactant gases, nitrogen is also supplied as an inert gas. It is often used to purge the reactant gases during shut down or start-up phases. The gas flow rates and absolute pressures can be maintained separately for the anode and the cathode. Both potentiostatic and galvanostatic operations are possible. Standard cell operation has the hydrogen and air flow rates maintained at a minimum stoichiometric ratio of 1.5 and 2.0, respectively. The pressure in both the anode and the cathode is maintained at 2.5 bar absolute and temperature is typically set at 160 °C. All freshly prepared test cells are subjected to a predefined set of test bench operations such as gradual increase in temperature and pressure. This brings about a conditioning of the cells. It assures an optimum and repeatable performance of the test cells.

A number of test cells are used to assure the reproducibility of the observed effect. Different test cells are used for different experiments, each having a slightly different cell current at around 0.6 V. The cell current loss after temperature cycle is observed in all the cells with varying degree, ranging from 5 to 15%.

3.2 Influence of Cooling Temperature

The primary effect observed after temperature cycling is the temporary loss of the cell current at operating conditions. First investigations are made into ascertaining the influence
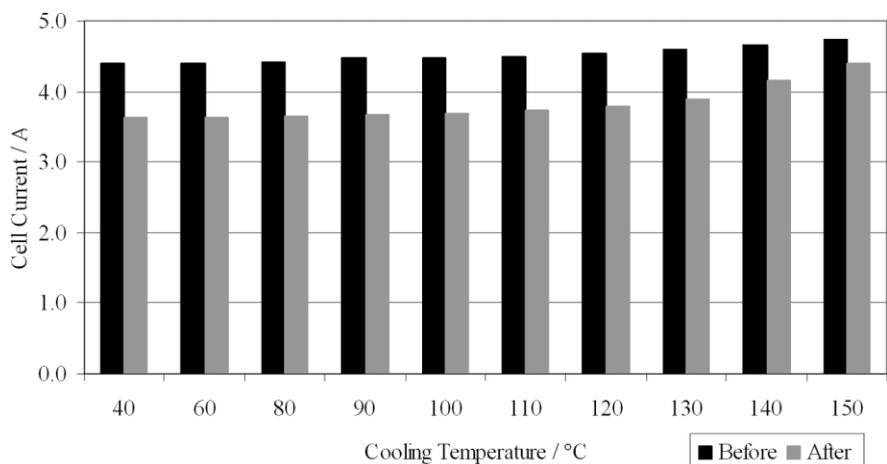
Fig. 4 Cell current at 160 °C after temperature cycling with different cooling temperature.

of the lower end of the temperature cycle. The test cell is put through a series of temperature cycles by varying the lower end of the cycle between 40 and 150 °C as shown in Figure 4. The cell current at 0.6 V and 160 °C is recorded before and after each temperature cycle. It is seen from Figure 4 that cooling temperatures below 110 °C have the same cell current loss. As the cooling temperature is increased above 120 °C, the magnitude of the cell current loss shows a decline. At a cooling temperature of 150 °C, a temperature cycle of just 10 °C brings about a small but definite cell current loss.

A fuel cell at a fixed operating point has a constant production of water molecules on the reaction sites of the cathode. These reaction sites are the platinum catalyst particle surfaces where ORR takes place. The neighboring sites on the catalyst surface are shared by adsorbed phosphoric acid and oxygen. The product water molecule desorbs from the reaction site thus making the site available for other oxygen molecules. At a given operating point, all three occurrences (phosphoric acid adsorption, oxygen adsorption, and product water desorption) are in quasi-equilibrium. Product water molecules that desorb from the reaction site diffuse through the thin electrolyte film to the surface, evaporate into the gas
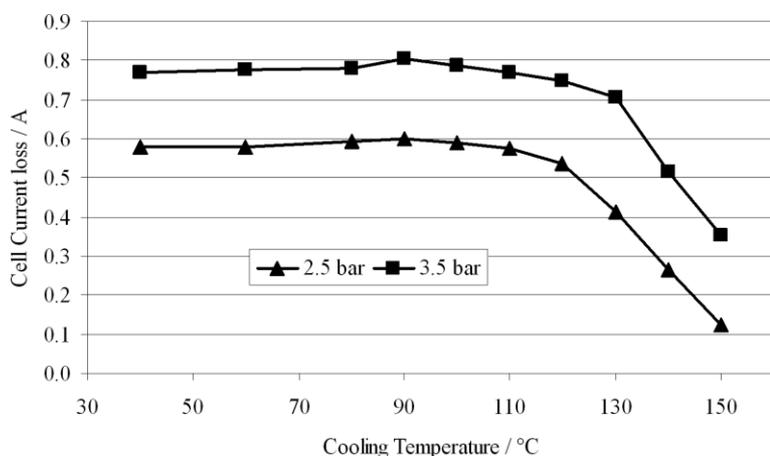
phase, and are then transported out through the GDL and flow field. This transport mechanism of product water is highly sensitive to temperature changes especially in regions of phase change from liquid to gas. At 2.5 bar operating pressure, the boiling point of water is approximately 129 °C. The observed cell current loss at various cooling temperatures shows a definite transition at 120 °C indicating a direct or indirect influence from the phase change of water in the system.

In order to test this theory, a test cell is put through the same series of temperature cycles for two operating pressures, 2.5 and 3.5 bar. The boiling point of water at 3.5 bar is 139 °C, which is 10 °C more than that at 2.5 bar. The absolute values of cell current losses against the cooling temperatures are plotted along in Figure 5. The losses are higher at 3.5 bar absolute pressure throughout the cooling temperature range and shows similar constant values at lower temperatures with the transition occurring at 130 °C. This 10 °C shift in the transition point correlates very well with the difference in the boiling point of water at the respective pressures. This observation indicates the possible influence of the equilibrium in the transport mechanism of the product water on the temporary cell current loss. The longer presence of product water on the catalyst surface at lower temperatures can cause interference to the adsorbate equilibrium. This effect is increasing with lowering temperature until the dew point is reached, beyond which the cell current loss after temperature cycle is seen constant.

The direct result of cell current loss can be caused by a reduction in the adsorbed oxygen on the catalyst surface. As shown in Figure 3b, a decrease in temperature increases the surface coverage of phosphoric acid. Since all other operating parameters are kept constant during the temperature cycle, an increase in the adsorbed phosphoric acid (hysteresis) after the cycle can be the probable cause for lower availability of reaction sites for oxygen and, thereby, causing the cell current loss.

3.3 Influence of Cell Voltage

The cell current loss due to temperature cycling is immediately recovered after a short voltage spike (2–3 s) to OCV. If the temperature cycle brings about an increase in the adsorbed phosphoric acid molecule, a cell voltage spike should in effect restore or reduce the adsorbed phosphoric acid molecules back to its original value (as was before the temperature cycle). As seen in Figure 3a, increase in electrode potential beyond 0.8 V results in desorption of the adsorbed phosphoric acid. In order to understand the influence of cell voltage, the cell voltage spike is resolved in

Fig. 5 Influence of cooling temperatures at different operating pressures.

Fig. 6 Cell current recovery after cell voltage spikes.

Fig. 7 Influence of cell voltage on cell current recovery.

Fig. 8 Adsorbed phosphonic ion symmetries at (a) low and (b) high potentials [10].

However, the absolute increase before and after the voltage spike shows a slightly different behavior. Figure 7 plots the magnitude of the recovered cell current against the peak value of the cell voltage spikes. It is observed here, that the complete range of cell voltage spike produces a cell current recovery with the complete cell current loss recovered at near OCV. This does not correlate very well with the cell voltage influence on the surface coverage of phosphoric acid as seen earlier (Figure 3a), where the coverage shows rather an increase in adsorbed phosphoric acid until 0.8 V and then begins to descend right after. Nevertheless, it is seen here that the voltage spikes attempt to restore the original adsorbate equilibrium. The larger the voltage spike, the higher is the magnitude of recovery.

Nart and Iwasita (Figure 8) presented another interesting approach on this matter. Similar to Habib and Bockris, *in situ* FTIR spectroscopy was used as an investigating technique to study the adsorption of phosphate species on platinum. Probable phosphate adsorbate symmetries depending on the cell voltage were presented. As seen in Figure 8a and b, the authors concluded that phosphoric acid adsorbs on platinum catalyst as a dihydrogen phosphate ($H_2PO_4^-$) ion. The probability of the C_{2v} symmetry where the ion adsorbs on platinum via the two single oxygen atoms is higher at cell voltages below 0.8 V. At higher voltages, the probability of having the Cs symmetry of the adsorbed ion is higher. The $H_2PO_4^-$ ion in this case is adsorbed on the platinum surface by one single oxygen atom.

At this stage it still remains unclear how exactly such changes in the symmetry of the adsorbed phosphonic ions due to changes in cell voltage can bring about the cell current recovery. However, the preliminary work presented here, provides a good starting point for future detailed investigations.

3.4 Cell Degradation Effects

The observed phenomenon in the HT PEM fuel cells is thought to be influenced directly by the adsorbate behavior on the surface of the platinum catalyst particles. Along with the freshly prepared test cells, older test fuel cells that have undergone long-term degradation tests (>300 h) are also tested for this phenomenon. These test cells also exhibit the same behavior after the temperature cycle but have a much larger (3–5 times) temporary cell current loss in comparison to the freshly prepared test cells. As expected, after a voltage spike the cell current instantaneously returns to its cell current value before the temperature cycle.

smaller steps. After each temperature cycle at 0.6 V, the cell voltage is spiked to an incremental value. The cell current before and after the voltage spike is recorded and plotted in Figure 6. It is observed here that a +0.05 voltage spike (to the peak value of 0.65 V) after a temperature cycle produces a small but definite recovery of the cell current. This trend increases with increasing cell voltage spikes until 0.85 V, beyond which the cell current recovery seems very nominal.

In order to make a reliable comparison between the two types of cells, the phenomenon is first tested on a freshly prepared test cell. The same cell is then put through a series of temperature and voltage cycles over 200 h. At certain time intervals, the magnitude of the cell current is recorded, a temperature cycle is performed and temporary cell current loss is measured. The results are plotted in Figure 9.

It is observed here that with the ageing of the test cell, its performance drops gradually. The cell current loss after temperature cycling, however, increases with time until about 250 h of testing, beyond which it stabilizes and further on even decreases at around 300 h. Based on transmission electron microscopy (TEM) and X-ray diffraction (XRD) results on the freshly prepared catalyst, the platinum particle size is estimated to be in the range of 3–4 nm. The older test cell catalyst shows an increase in particle size of up to 9 nm. This increase in platinum particle size after ageing shows very good agreements with similar tests performed on HT PEM fuel cell catalysts [11–13]. The general agreement is that the drop of cell performance is associated with the loss in the electrochemically active surface area largely due to particle size growth. With this consideration, it can be stated that increasing platinum particle size tends to increase the cell current loss after temperature cycles. However, toward the end of the shown ageing test, this trend ceases. This would imply one or both of the following. The influence of the increasing reaction surface area on the cell current loss ceases beyond a certain particle growth. And the platinum particle growth itself is limited to a certain stable size, and, thereby, limits the increase in the reaction surface area per particle. This observation strongly supports the theory that the observed phenomenon is directly related to the occurrences on the catalyst surface and that the size of the platinum particle surface area (and not the total surface area) itself plays an important role.
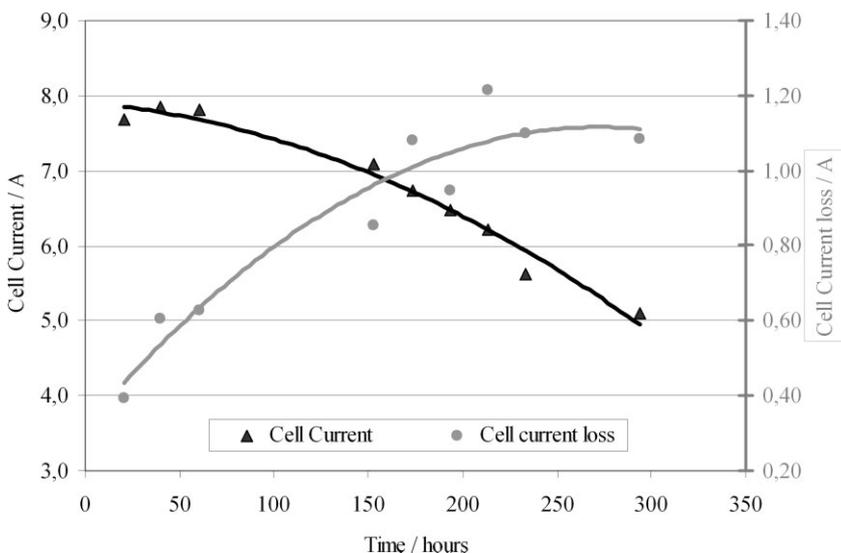
4 Hypothesis

Based on the preliminary investigations into the observed phenomenon, a hypothesis is presented. The description follows the phenomenon as designated in Figure 1.

4.1 A to B: Adsorbate Orientation

The cell current output is largely determined by the cathode side ORR at higher cell voltages. The electrochemically active platinum catalyst particles have three competing adsorbate species, namely phosphoric acid, oxygen, and product water. For a given set of operating conditions for the HT PEM fuel cell, there exists a (quasi) equilibrium between these adsorbates on each of the reaction surfaces. While the number of adsorbed phosphate ions stays constant, the adsorbed oxygen reacts to form water and the product water desorbs to vacate the reaction site for the next oxygen molecule adsorption. Reducing the temperature while keeping all other operating parameters constant induces a different equilibrium of the adsorbates. This is largely due to the temperature-dependent adsorption behavior of phosphoric acid on platinum catalyst. The adsorbate orientation is influenced directly or indirectly by the transport mechanism of product water. The observed cell current during cooling is determined by temperature dependence of the reaction kinetics as well as the concentration of the adsorbed oxygen at the given temperature.

4.2 B to C: Adsorbate Disorientation

Increasing of the fuel cell temperature back to its operating temperature shows a gradual increase in the cell current. This increase in cell current stops short of the value before the temperature cycle. Since the operating conditions are identical before and after the cycle, a reduction in the oxygen adsorbates is the only plausible explanation for the current loss. This is possible if the adsorbed phosphoric acid molecules would exhibit a hysteresis, i.e., the adsorbed phosphoric acid will not recover to its original value at operating temperature after the temperature cycle. This change in adsorbate orientation before and after the cycle is possibly due to the interference of product water molecules with the adsorbed phosphoric acid.

4.3 C to D: Adsorbate Reorientation

The fuel cell recovers the temporary cell current loss instantaneously when subjected to an OCV for a couple of seconds. The fuel cell voltage has a definite influence on the adsorption of phosphoric acid molecules on the platinum catalyst. A spike in cell voltage

Fig. 9 Cell current loss with respect to ageing.

induces an immediate change in the adsorbate symmetry of the phosphate ion. This essentially provides the possibility for the adsorbates to return to their original orientation, which is signaled by the return of the cell current to its value before the temperature cycle.

5 Conclusion

The occurrence of the cell current hysteresis in a HT PEM fuel cell after a temperature cycle has been investigated. The temporary cell current loss is recovered when OCV is applied. Experiments performed by varying cooling temperature show the possibility of the product water transport mechanism influencing the magnitude of the cell current loss. This argument is further strengthened by the experiments performed at two different pressures. The cell current loss is recovered when the cell voltage is spiked to OCV. Both temperature and cell voltage influence the adsorption of phosphoric acid molecules on platinum catalyst. The origin of this occurrence is therefore expected to be on the electrochemically active platinum reaction surfaces. Hysteresis in the adsorbed phosphoric acid due to a temperature cycle seems to be the reason for the cell current loss. A possible reorientation of the adsorbates when subjected to a cell voltage spike explains the recovery of the cell current loss. Increase in platinum particle size increases the temporary cell current loss. This indicates a proportional relationship between the changes in adsorbate orientation on the platinum particle surface and the reaction surface area of a particle.

The authors present a hypothesis for the observed phenomenon, which can be used for further detailed investigations. This phenomenon provides a new possibility to acquire valuable insights into the functioning of phosphoric acid-based fuel cells.

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