



Short communication

## Effects of crossover hydrogen on platinum dissolution and agglomeration

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## ABSTRACT

The durability of catalysts in the polymer-electrolyte membrane fuel cell (PEMFC) is identified as a critical limiting factor for wide commercialization of fuel cells. Even though much progress has been made in understanding the degradation mechanisms, the phenomena of Pt dissolution and agglomeration and their contributing factors are not fully understood. In the present investigation, the effects of crossover hydrogen on Pt degradation are studied using an accelerated stress test (AST). The end-of-test (EOT) membrane-electrode-assemblies (MEAs) were characterized by X-ray diffraction (XRD), scanning-electron microscopy (SEM), and energy-dispersive X-ray (EDX). The results provided mechanistic understanding of Pt dissolution and agglomeration: Pt growth and agglomeration were found to be less severe with more crossover hydrogen due likely to the chemical reduction of Pt oxides by crossover hydrogen and the subsequently decrease in the amount of Pt ions formed via the oxide pathway.

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### 1. Introduction

The polymer-electrolyte membrane fuel cell (PEMFC) is a promising and clean alternative to conventional technologies in various applications, including light and heavy-duty vehicles, materials handling, back-up power for telecommunications, stationary cogeneration, and distributed power systems. In order for the fuel cell technology to be widely adopted, the membrane-electrode-assembly (MEA) needs to possess long-term durability: the current durability targets for PEMFCs are 40,000 and 5000 h for stationary and automotive applications, respectively [1].

Cathode catalyst degradation, in particular, has been studied and reviewed extensively [2–13]. Catalyst degradation, which can cause severe irreversible performance impacts, is caused by any or combinations of Pt loss [2–6], contamination [7–13], and support corrosion. Pt loss, which leads to reduction in electrochemically active surface area, can arise from Pt dissolution, detachment from support, and agglomeration. Pt agglomeration is generally accepted to be the result of Ostwald ripening, crystal migration/coalescence, and dissolution/reprecipitation [2,4]. It is known that operating conditions, such as temperature, relative humidity (RH), and upper potential limit (UPL) have significant impacts on the Pt catalyst degradation mechanisms. Even though much progress has been made, the degradation mechanisms and contributing factors are not fully understood. In particular, the effects of crossover hydrogen, which is a function of hydrogen partial pressure, have not been extensively studied. Yasuda et al. have previously studied the

impacts of crossover hydrogen on the location of the Pt band formed in the membrane after Pt dissolution [14]. The Pt band or platinum-in-the-membrane (PITM) was shown to be located closer to the anode under lower hydrogen partial pressure conditions [14]. Similarly, Zhang et al. examined the effects of hydrogen and oxygen partial pressures on Pt precipitation within the membrane [15], and developed a simple model to estimate the location of the PITM band (Eq. (1)). Neither of these studies evaluated the impact on the cathode catalyst layer.

$$\delta_{\text{PITM}} = \frac{K_{\text{H}_2} p_{\text{H}_2} \delta_{\text{Membrane}}}{K_{\text{H}_2} p_{\text{H}_2} + 2K_{\text{O}_2} p_{\text{O}_2}} \quad (1)$$

$\delta_{\text{PITM}}$  is the PITM location,  $\delta_{\text{Membrane}}$  is the membrane thickness,  $K$  is the membrane gas permeability, and  $p$  is the gas partial pressure.

In contrast, Holby et al. studied the influence of crossover hydrogen on the stability of Pt nanoparticles via a theoretical approach [16]. With crossover hydrogen, the Pt degradation mechanism under potentiostatic dwell of 0.95 V was demonstrated to shift from coarsening to Pt loss. However, the crossover hydrogen effects on Pt degradation and the subsequent impacts on the cathode catalyst layer have not been experimentally evaluated and reported. In the present study, the effects of crossover hydrogen on Pt dissolution and agglomeration are investigated in fuel cell stacks under dynamic cycling conditions that simulate fuel cell system start-ups and shutdowns.

### 2. Experimental

Accelerated stress tests (ASTs) were carried out using a 5-cell stack with active area of 45 cm<sup>2</sup> per cell. The cathode and anode catalyst loadings (Pt/C) were 0.4 and 0.1 mg Pt cm<sup>-2</sup>, respectively.

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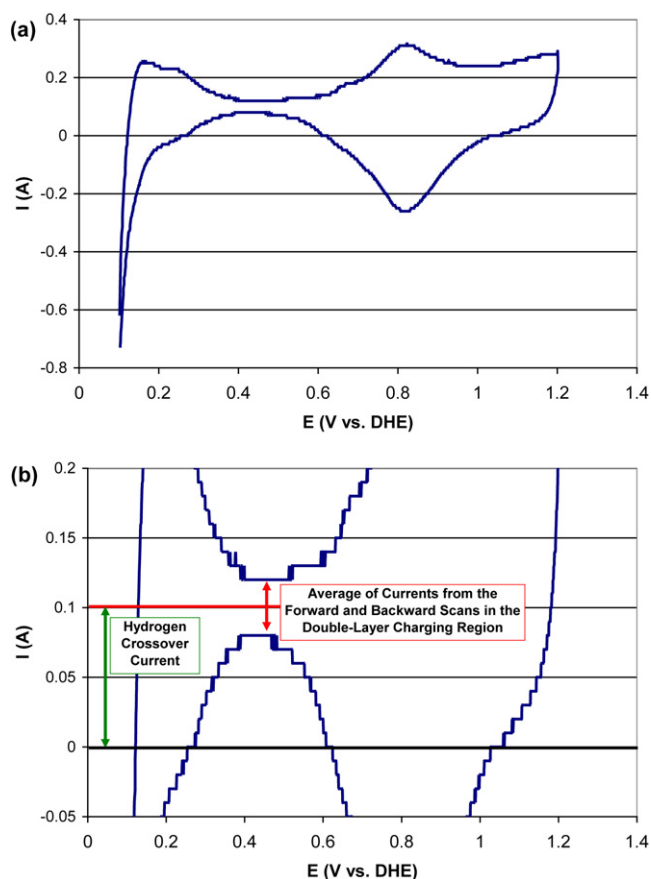


Fig. 1. Hydrogen crossover current estimation: (a) typical cathode CV; (b) schematic of estimation method (zoomed view of cathode CV). Scan rate:  $20 \text{ mV s}^{-1}$ .

The AST conditions were  $80^\circ\text{C}$ , 1.3 bar pressure, 100% RH, 1.2 V UPL, and 0.6 V lower potential limit (LPL). The polarization curves were measured at  $75^\circ\text{C}$ , 1.3 bar pressure, and 100% RH. The electrochemically active area of Pt of each cell was individually measured by CO-stripping cyclic voltammetry (CV). The measurements were performed in situ, using a PAR Model 263A potentiostat connected to a 10 A Kepco power booster with the CorrWare software, as illustrated in previous publications [12,13]. The average of the currents measured in the forward and backward scans in the double-layer charging region was taken as the hydrogen crossover current (see Fig. 1 for schematic of estimation method). All gases used were supplied by Praxair.

In addition to in situ electrochemical measurements, the end-of-test (EOT) cathode catalysts and MEAs were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray (EDX) to determine the catalyst crystallite size, location of PITM, and composition, respectively. XRD spectra were acquired using a D8ADVANCE X-ray diffractometer (Bruker Axs, Inc.) with a  $\text{CuK}\alpha 1$  X-ray source scanning from  $10^\circ$  to  $90^\circ$  at an angle increment of  $0.02^\circ/\text{step}$ . SEM and EDX experiments were carried out using the Phillips XL30 ESEM TMP.

### 3. Results and discussion

#### 3.1. Hydrogen crossover as a function of anode hydrogen concentration

The effect of anode hydrogen concentration on hydrogen crossover was first evaluated to determine how much hydrogen crossover could be reduced. The estimated hydrogen crossover currents with 20, 60, and 100% hydrogen (balanced with nitrogen) on

**Table 1**  
Hydrogen crossover currents at different anode hydrogen concentrations.

Hydrogen concentration (vol%)	Hydrogen crossover current ( $\text{mA cm}^{-2}$ )
20	$0 \pm 0.1$
60	$1.1 \pm 0.1$
100	$2.3 \pm 0.1$

the anode are shown in Table 1. The hydrogen crossover currents were found to be  $0 \pm 0.1$ ,  $1.1 \pm 0.1$ , and  $2.3 \pm 0.1 \text{ mA cm}^{-2}$ , respectively. In the case of 20% hydrogen, the hydrogen crossover current was lower than the estimation threshold of  $0.1 \text{ mA cm}^{-2}$ . Therefore, hydrogen crossover was very minor in this case; however, it should not be completely ruled out. The results indicate that a wide range of hydrogen crossover was achieved by adjusting the anode hydrogen volume fraction; hence, the effects of crossover hydrogen on cathode voltage degradation could be studied by varying the anode hydrogen concentration.

#### 3.2. Effects of crossover hydrogen on cathode degradation

Using the AST described in Section 2, MEAs were cycled 4700 times (EOT) to cause Pt degradation. The SEM cross-sections of EOT MEAs cycled under different hydrogen crossover conditions are shown in Fig. 2.

Firstly, it is evident that the location of PITM shifted towards the anode with decreasing hydrogen crossover. This is expected based on theory and the studies carried out by Yasuda et al. and Zhang et al. [14,15]. In fact, using the simple model developed by Zhang et al. [15] (see Eq. (1)), the PITM locations with 20%, 60%, and 100% hydrogen were predicted to be approximately 15, 23, and  $26 \mu\text{m}$  from the anode, respectively, identical to the SEM measurements (Table 2).

Secondly, based on EDX, the amount of PITM and Pt remaining in the cathode catalyst layer were found to be virtually identical for the different tests. The results imply that the net ionic Pt flux going towards the anode was very similar regardless of crossover hydrogen. In conjunction with the longer diffusion path required to deposit as PITM at lower hydrogen crossover, the similar ionic Pt flux observed at different degrees of crossover hydrogen signi-

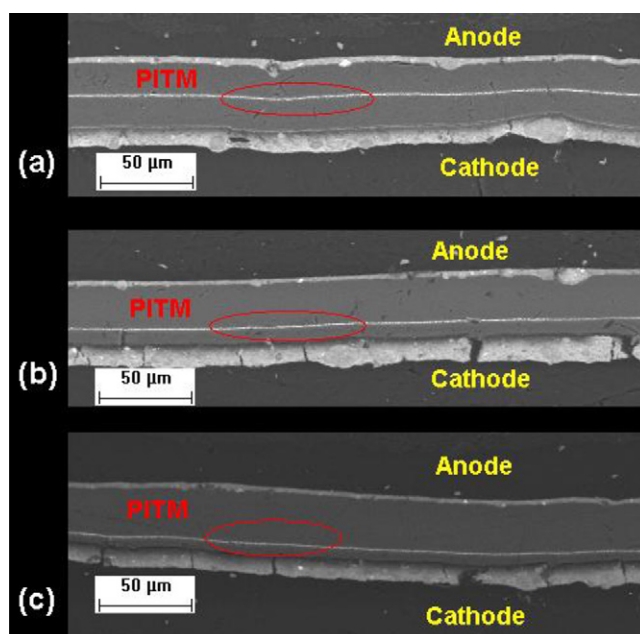


Fig. 2. SEM cross-sections of MEAs at EOT. Hydrogen crossover currents: (a)  $0 \text{ mA cm}^{-2}$ ; (b)  $1.1 \text{ mA cm}^{-2}$ ; (c)  $2.3 \text{ mA cm}^{-2}$ .

**Table 2**

PITM locations of EOT MEAs stress-tested at different anode hydrogen concentrations.

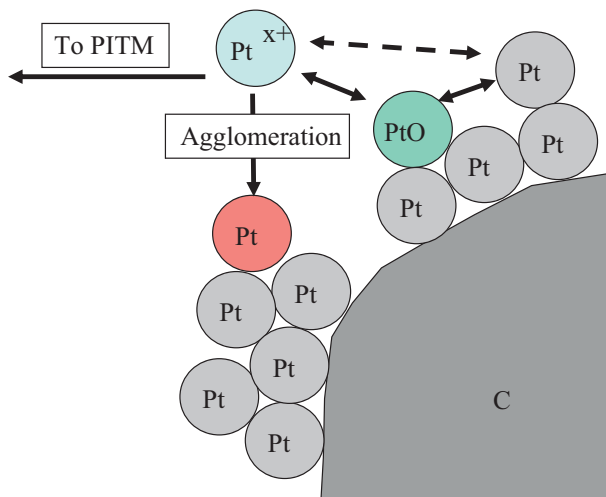
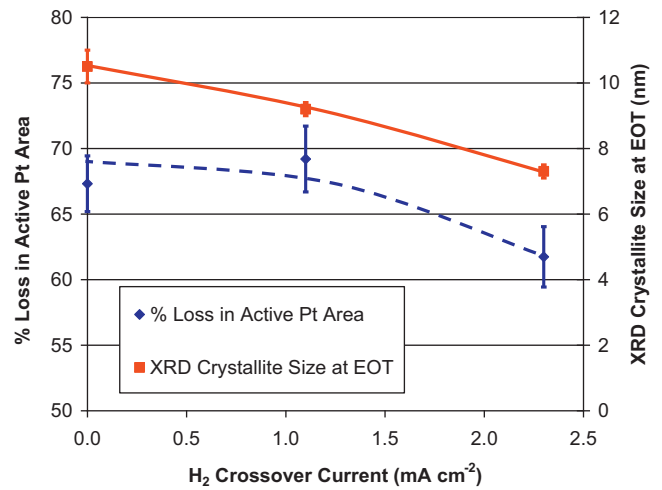
Hydrogen concentration (vol%)	Predicted location of PITM ( $\mu\text{m}$ from anode)	Location of PITM from SEM ( $\mu\text{m}$ from anode)
20	15	15
60	23	23
100	26	26

ties that, based on Fick's Law of diffusion, the local concentration of Pt ions was higher at the cathode catalyst layer when there was less crossover hydrogen. It is hypothesized that crossover hydrogen may chemically reduce Pt oxides (Reaction 1) and decrease the amount of Pt ions formed via the oxide pathway (Reaction 2).



This suggests that Pt agglomeration would be more severe in the case with less crossover hydrogen since there were more Pt ions available for deposition and crystallite growth. In addition, the results also imply that under the current cycling conditions, Pt ion formation proceeds predominantly through the Pt oxide pathway (see Fig. 3 for schematic). The notion is supported by the relative % loss in active Pt area and XRD crystallite size at EOT. As shown in Fig. 4, it is evident that Pt growth increased with decreasing crossover hydrogen as shown by the larger crystallite size and higher Pt area loss.

In terms of Pt growth, the results agreed well with the model predictions by Holby et al. [16]. However, in contrast to the modelling results, no additional Pt mass loss was observed in the case with less crossover hydrogen. As discussed above, the amount of Pt remaining at EOT in the present study was found to be similar regardless of hydrogen crossover. The discrepancy was likely due to the difference in degradation profiles employed in the two studies. In the modelling work presented by Holby et al., the cathode was held at a constant potential of 0.95 V as compared to cycling between 0.6 and 1.2 V in the present study. In the case of constant potential dwell of 0.95 V, the presence of hydrogen may chemically reduce the cathode Pt oxides and ions that are formed electrochemically due to the high potential, leading to a scenario that is similar to potential cycling. It is well known that potential cycling causes more Pt loss and degradation as compared to potentiostatic dwelling [4]. In the case of electrochemical potential cycling, since the catalysts already experience surface oxidation/reduction

**Fig. 3.** Schematic of Pt dissolution mechanism.**Fig. 4.** Effect of crossover hydrogen on % loss in active Pt area and XRD crystallite size of cathode catalysts at EOT.**Table 3**

Degradation rates of MEAs stress-tested at different anode hydrogen concentrations.

Hydrogen concentration (vol%)	Degradation rate at $0.67 \text{ A cm}^{-2}$ ( $\mu\text{V cycle}^{-1}$ )
20	$11 \pm 2$
60	$13 \pm 2$
100	$13 \pm 2$

even without the presence of hydrogen, the influence of additional chemical reduction by hydrogen on overall Pt loss may be overshadowed. Even though the overall Pt loss was not affected by crossover hydrogen in the present study, Pt dissolution and agglomeration were clearly impacted by the coupled effects of partial pressure of hydrogen in the membrane and crossover hydrogen.

The degree of carbon surface oxidation, which has significant influence on non-kinetic losses, was also assessed. Based on the changes in double-layer capacitance, the degree of carbon surface oxidation was found to be negligible and virtually identical at EOT for the various tests [17]. The results indicate that crossover hydrogen has no impact on carbon surface oxidation and corrosion.

Additionally, the cell performance losses after AST were evaluated. It was found that the stack performance losses were not significantly different (within experimental variability) at EOT. The degradation rates at  $0.67 \text{ A cm}^{-2}$  with 20%, 60%, and 100% hydrogen were found to be  $11 \pm 2$ ,  $13 \pm 2$ , and  $13 \pm 2 \mu\text{V cycle}^{-1}$ , respectively (Table 3). This is somewhat expected as performance losses are often dominated by non-kinetic losses and that the active Pt surface area losses were not vastly different.

#### 4. Conclusions

The effects of crossover hydrogen on Pt dissolution and agglomeration were evaluated with an AST carried out using a 5-cell stack. The experimental results provided mechanistic insights of Pt dissolution and agglomeration. The effects of crossover hydrogen on Pt degradation were hypothesized to be as follows:

- (1) Crossover hydrogen chemically reduces Pt oxides and subsequently decreases the amount of Pt ions formed via the oxide pathway.
- (2) Hence, with less crossover hydrogen, the concentration of Pt ions in the cathode becomes higher and subsequently leads to more Pt growth and agglomeration, in agreement with the relative XRD crystallite sizes and active surface area loss by CO stripping.

- (3) At the same time, PITM forms closer to the anode, concurring with theory and SEM observations.
- (4) Based on Fick's Law of diffusion, the higher Pt ion concentration may counterbalance the longer Pt ion diffusion path. Therefore, the resulting ionic Pt flux was comparable regardless of hydrogen crossover. Consequently, the respective amount of PITM was almost identical, in agreement with the EDX results.

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