

Effects of Interim Cyclic Voltammetry on Pt/CB Catalyst Degradation during Start-up/shutdown Cycling Evaluation

Young-Chul Park,^a Katsuyoshi Kakinuma,^a
Masanori Hara,^a Makoto Uchida,^a
Hiroyuki Uchida,^{a,b} and Masahiro Watanabe^a

^a Fuel Cell Nanomaterials Center, University of Yamanashi, 6-43 Miyamae, Kofu 400-0021, Japan

^b Clean Energy Research Center, University of Yamanashi, 4 Takeda, Kofu 400-8511, Japan

We investigated the effects of interim cyclic voltammetry (CV) on Pt/CB catalyst degradation and Pt-catalyzed carbon corrosion during start-up/shutdown evaluation. The CV measurements, which are generally conducted after a certain number of potential cycles to evaluate the electrochemically active surface area (ECSA) of Pt catalysts, result in depassivation of the passive layer formed on Pt particles during the cycling tests; this allows the platinum to again catalyze the carbon corrosion effectively during the potential cycling. This phenomenon causes more severe corrosion of the CB support. The measured ECSA loss, cycle half-life $N_{1/2}$ (N value at which the ECSA value was estimated to reach 1/2 of the initial value) and IR -free polarization curves show that the potential cycling, followed by intermittent CV measurements on the same electrode, termed consecutive cycling, brings about severe lifetime reduction and cell performance degradation of the Pt/CB catalyst.

The Raman spectra and quinone-hydroquinone (Q-HQ) oxidation current both support the idea that this degradation can be ascribed to severe corrosion of the CB support by the consecutive cycling. In addition, SEM and TEM images confirm that the interim CV measurements lead to severe degradation of the Pt/CB catalyst due to dissolution of platinum, detachment of Pt particles and carbon support corrosion.

Figure 1 exhibits the ECSA changes of the Pt/CB catalyst by the cycle testing modes. As shown in Fig. 1, the consecutive cycling mode showed a high reduction rate of the ECSA, the values decreasing rapidly in proportion to $\log N$ from 100 to 10000 cycles. In contrast, the decrease in ECSA of separate, individual electrodes that were subjected only to potential cycling, with no CV, was quite gradual, with only moderate decreases up to 3000 cycles. Specifically, most of the decrease in ECSA can be ascribed to the activating effect of the CV measurements. After 10,000 potential cycles, the ECSA values for the consecutive and individual cycling modes were $28.8 \text{ m}^2 \text{ g}^{-1}$ and $45.5 \text{ m}^2 \text{ g}^{-1}$, respectively. The normalized ECSA losses corresponded to 53.0 % and 27.2 %, respectively. The cycle half-life $N_{1/2}$ for the Pt/CB catalyst in the consecutive cycling mode was estimated to be approximately 5000 cycles, whereas it is difficult to estimate $N_{1/2}$ for the individual cycling mode (> 10000 cycles) in this study.

The differences in the ECSA decrease rates and cycle half-lives $N_{1/2}$ may be due to the interim CV measurements during the consecutive cycling, which was characterized by the hydrogen adsorption/desorption (ECSA evaluation in the 0.075-0.4 V range) and oxygen-related reactions (formation and reduction of the Pt oxides: PtO, PtO₂ and Pt-O_{ad} in the 0.5-1.0 V range). According to Dam et al.,¹ the formation of passivating surface oxides on Pt particles leads to the saturation of the

platinum dissolution rate at potentials of approximately 1.15 V, and even to a suppression of the platinum dissolution at potentials of approximately 1.4 V. Sugawara et al.² reported that the platinum dissolution reaches a maximum at 1.1 V. Meyers et al.³ also presented that the Pt surface is fully oxidized and is covered by a complete monolayer of oxide in the high potential region. Furthermore, the formation of passivating surface oxides on Pt particles can suppress the Pt catalytic effect on the corrosion reaction of the CB support.⁴ Therefore, the lower ECSA losses of the individual cycling can be ascribed to the limited platinum dissolution and carbon corrosion reaction by passivating surface oxides formed on Pt particles during the cycling tests. On the other hand, the higher ECSA losses of the consecutive cycling can result from severe platinum dissolution and corrosion of the CB support by the surface oxidation-reduction state of the Pt particles during the start-up/shutdown cycling and interim CV measurements.

This result suggests that the individual cycling mode, operating only in the potential range in which the platinum is oxidized, can lead to moderate degradation of the Pt/CB catalyst, whereas the consecutive cycling with interim CV measurements, including potentials (cathodic sweep in the potential region between 0.5 V and 0.075 V) at which the Pt oxides can be reduced,⁵ can bring about severe degradation of the Pt/CB catalyst.

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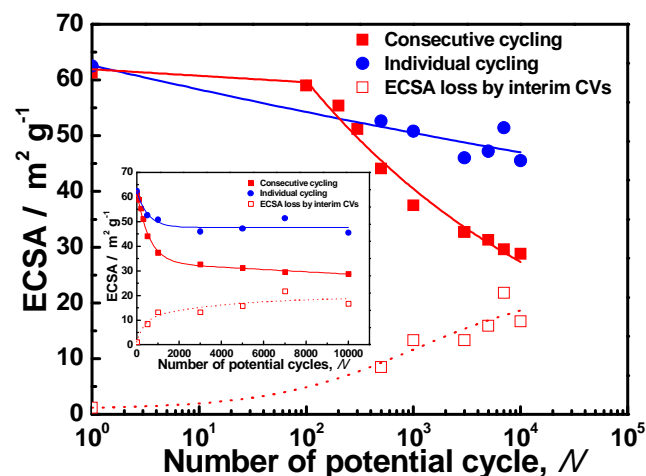


Fig. 1. Changes of ECSA values of Pt/CB catalyst by the consecutive cycling and individual cycling modes.

References

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