We investigated the electrochemical stability of a Pt/Pd(111) model core–shell structure for oxygen reduction reaction catalysts in 0.1 M HClO₄ at 80 °C by performing potential cycles (PCs) between 0.6 and x V vs. RHE (x = 0.8–1.0; x-PCs). Pristine Pt/Pd(111) shows an ORR activity four times higher than that of Pt(111), which considerably decreased after 5000 cycles of 0.9- and 1.0 V-PCs and remained nearly unchanged for the 0.8- and 0.85 V-PCs samples. These results suggest that the atomic-scale structural changes at the Pt/Pd interface that depend on PC windows determine the durability of Pt–Pt core–shell structures.

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agglomerated particle-like structures that were 20-nm wide and 3-
nm high. These results indicate that the ULPs of the square-wave
PCs, i.e., surface oxidation, including oxygen or OH-related species
adsorptions, strongly influence the EC stability of the Pt/Pd(111) sam-
ple. The deconvoluted LEIS spectra show that the signals are due to
surface Pd atoms, irrespective of the ULPs, indicating that the topmost
surfaces comprise Pt/Pd alloys instead of pure Pt. Furthermore, the
surface Pd/Pt atomic ratio of the 0.9V-PCs sample is higher than that
of the 0.8V-PCs sample by approximately 30 \%. Therefore, the top-
most surface Pd/Pt atomic ratios are strongly correlated with the ORR
deactivation process during the PCs loadings, which is accompanied
by an increase in the Pd/Pt atomic ratios. Nevertheless, the observed
structural changes (STM and LEIS) are consistent with the increase
in the charge of the CVs (Figure 4a).

To the best of our knowledge, very few studies related to the ef-
flect of the electrolyte temperature on EC stabilities of Pt-based ORR
catalysts have been reported. Ohma et al. investigated the influence of
potential ranges on commercial Pt/C catalysts in an accelerated dura-
bility test (ADT) and demonstrated that the electrochemical surface
areas (ECSA) significantly decreased after 15k cycles of the ADT
with ULPs over 0.90 V.\(^7\) Xing et al. reported that increasing solution
temperatures cause lower shifts of the onset potentials for the oxi-
dation reaction of the polycrystalline Pt surface, resulting in larger
dissolution of the Pt atoms.\(^8\) The degradation behaviors of Pt/Pd(111)
analyzed in this study seem to be more prominent than the aforemen-
tioned results of pure Pt catalysts. Accordingly, because Pd exhibits
much lower activity than Pt, the activity degradations of the Pt/Pd(111)
sample should be governed by atomic-level surface structural changes
induced by the electrochemical redox reactions and following inter-
diffusion of the Pt and Pd atoms located near the surface regions.\(^9\)

Two possible origins of structural (STM) and compositional (LEIS)
changes of Pt/Pd(111) near surface region can be considered. One
is a decrease in the effective thickness of the Pt(111)-surface lay-
ners induced by the aggregation of surface Pt atoms during the PC
loadings. Actually, Conway proposed a place-exchange reaction of
oxygen species and that surface Pt atoms could cause atomic-level
surface roughing of the Pt electrode.\(^10\) Another is oxygen adsorption-
induced surface segregation of the substrate Pd atoms. It has been
reported that more oxophilic metals tend to segregate to the topmost
surface of Pt shell layers when oxygen adsorbs on Pt/M bimetallic al-
loy surfaces.\(^11\) Hence, surface roughening of Pt shell layers as well as
surface segregation of Pd atoms during the PC loadings are correlated
with the deactivation of Pt/Pd(111). Once the substrate Pd atoms seg-
regate to the topmost surface, they would immediately dissolve into
the electrolyte, thereby leading to extreme activity decrease for ULPs
above 0.9 V. Nonetheless, although further atomic-scale investigations
are required for clarifying atomic-level degradation mechanisms of
Pt/Pd(111) core–shell model structures, Pt and Pd near-surface be-
haviors at a given ULP determine the EC stability, i.e., the durability
of the actual Pd–Pt core–shell ORR catalysts.

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**Figure 1.** Surface structure and initial electrochemical properties of Pt/Pd(111): (a) UHV-STM image (inset: RHEED pattern), (b) LEIS spectrum, (c) cyclic voltammogram, and (d) \(i_k\) values for ORR at 0.9 V vs. RHE.

**Figure 2.** LSV curves of Pt/Pd(111) for ORR recorded at 1600 rpm in 0.1 M HClO\(_4\) at RT and after 1000 PCs at both RT and 80\(^°\)C.

**Figure 3.** Changes in the \(i_k\) values of Pt/Pd(111) during PCs with different ULPs at 80\(^°\)C.
Summary

We investigated the EC stabilities of 4 ML-thick Pt deposited on Pd(111) model core–shell structures during PCs with various potential windows in 0.1 M HClO₄ at 80°C. The initial ORR activity was estimated to be approximately four times greater than that of clean Pt(111). While the 1.0V-PCs Pt/Pd(111) sample was remarkably deactivated, lowering the ULPs of the PCs suppressed the activity deterioration. Specifically, 0.85- and 0.8V-PCs Pt/Pd(111) samples showed activities of approximately 90% and 120%, respectively, for the pristine sample activity, even after 5000 cycles. These results suggest that changes in the Pt/Pd interfacial structures during PCs determine the ORR durability of Pd–Pt core–shell catalysts.

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