Highly Durable and Active PtCo Alloy/Graphitized Carbon Black Cathode Catalysts by Controlled Deposition of Stabilized Pt Skin Layers

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We have developed a new, facile solution-phase method for the controlled deposition of targeted numbers (1 to 4) of Pt-skin layers on PtCo alloy nanoparticle surfaces that have already been heat-treated in the presence of H₂ to form an initial single Pt layer, both processes being carried out with the particles on a carbon support. In particular, we report the deposition of an additional single atomic layer of Pt to produce a stabilized dual-layer Pt-skin formed on Co-enriched nanocore surfaces, which were dispersed on graphitized carbon black (Pt₂AL–PtCo₇/25/GCB). This catalyst was found to provide high mass-activity, three times greater than that of a commercial Pt/CB catalyst for the oxygen reduction reaction and distinctively high durability during standard potential-cycling test-protocols designed to simulate load changes and start/stop cycles in 0.1 M HClO₄ solution at 65 °C. This method is one of the simplest, most convenient possible approaches to obtain both high activity and high durability for cathode catalysts used in polymer electrolyte fuel cells.

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Manuscript submitted January 1, 2016; revised manuscript received February 16, 2016. Published March 3, 2016.

It has been shown that the electrochemical oxygen reduction reaction (ORR) on Pt catalysts is enhanced by alloying with non-precious metals such as Fe, Co, and Ni, dependent on their composition. It has also been clearly demonstrated with X-ray photoelectron spectroscopy (XPS), in situ electrochemical quartz-crystal microbalance (EQCM) and in situ electrochemical scanning-tunnelling-microscope (EC-STM) measurements at sputtered Pt alloy electrodes that non-precious metal elements were leached out in acidic solution, followed by the spontaneous formation of an atomically flat “Pt-skin layer” on the alloy surface. The specific activity for the ORR on the Pt-skin layer has been enhanced by an electronic structure modified by that of the underlying alloy. For polymer electrolyte fuel cells (PEFCs), nano-sized platinum and platinum-based alloy (Pt-M) particles dispersed on high surface area carbon black (CB) support materials (Pt/CB, Pt-M/CB) have been used as high-efficiency electrocatalysts. The properties of these nanoparticle cathode catalysts depend on their size and/or composition, shape, and distribution. However, the ORR activity and the durability of these nanoparticles are still insufficient for widespread utilization of PEFCs in applications such as power generation units for fuel cell vehicles (FCVs) and residential co-generation systems. In practical PEFCs (operated at 60–90 °C), two typical degradation modes of the cathode catalysts have been recognized: (1) Pt dissolution-redeposition caused by oxidation/reduction reactions at Pt particle surfaces during frequent load-cycling, and (2) corrosion of the carbon support from positive potential excursions during start/stop or fuel starvation, resulting in losses of Pt active surface area due to detachment of Pt nanoparticles from the support and subsequent agglomeration.

The optimum particle size or shape of Pt or Pt-M alloy nanoparticles still has not been conclusively determined, because particles obtained by conventional methods (e.g., colloidal and combinations of impregnation and heat treatment) usually exhibit a broad distribution of sizes or compositions, which strongly affect the catalytic activity and durability.

In order to protect the underlying Pt-based alloy from corrosion and maintain the modified electronic structure of the Pt-skin, Pt-based core-shell type nanoparticles have been proposed as promising candidates for highly active, durable catalysts during the past several years. Such a “Pt-skin layer” structure and corresponding catalysis on alloy nanoparticle catalysts were first proposed by us11 and have been used in our extended studies (see, e.g., Refs. 2–6) for the ORR and also for the H₂ oxidation reaction (HOR).12,13 We will henceforth simplify the terminology by using the term “Pt-skin” or “skin layer” to denote both “Pt-skin layer” and “Pt shell.” These Pt-skin structures have been prepared mainly by three techniques, (1) underpotential deposition (UPD) of a copper monolayer (Cu(UPD)) on core particles, followed by a galvanic replacement reaction with a Pt monolayer,14,15 ii) chemical leaching (dealloying) of the non-noble metal, followed by high-temperature annealing,16,17 and iii) galvanic replacement reaction of the surface non-precious metal with Pt. In such methods, the surface is not always perfectly covered with the Pt-skin, so that it is difficult to control the local structure, composition, and particle size. Consequently, the durability has not been as high as expected.

Recently, we have developed an advanced method for preparing Pt/CB and Pt-M/CB catalysts, the “nanocapsule” method, which provides monodisperse nanoparticles with well controlled size and composition.19 Nevertheless, the alloy particles prepared by this method still exhibit de-alloying in hot acid solution at practical operating temperatures (>70 °C). Accordingly, the performances of Pt alloys have exhibited deterioration to a level equivalent to that of pure Pt after operation under such conditions.20 More recently, we have succeeded in preparing multi-atomic layers of Pt-skin (PtMAL) on PtCo core-particles, which had well-controlled composition, particle size and Pt-layer thickness, supported on graphitized carbon black (2n-PtMAL–PtCo(GCB)) by applying the nanocapsule method in a stepwise fashion.21 This approach is not suitable for scale-up, however, due to the somewhat complicated procedure, as well as the deposition of a small amount of ultratine pure Pt particles (ca. 1.5 nm, < a few vol. %) separate from the core alloy surfaces. Nevertheless, the Pt-skin PtCo alloy structure stabilized in this way exhibited a several-fold higher durability and more than a two-fold higher mass activity, based on Pt weight initially loaded, for the ORR, compared with those of a commercial Pt/CB (denoted as c-Pt/CB) catalyst.

In the present research, we propose an ultimately simple solution-phase method for the preparation of precisely controlled, uniform Pt-skin layers on Pt-based alloy nanoparticles, i.e., simply by sparging 5% H₂ (N₂ balance) into an aqueous suspension of a source core catalyst with the exact amount of dissolved H₂PtCl₆ required for the desired number of skin layers. Prior to this step, we heat-treated the Pt alloy nanoparticles in the presence of H₂ in order to form an initial single Pt atomic layer. We also report the electrochemical properties (ORR activity and durability) of the new Pt-skin catalysts.
New Concept of the Facile Preparation of Highly Active and Durable Electrocatalysts Consisting of Non-Precious Metal Core and Atomically Controlled Pt-Skin Layer

Pt-M alloy/CB catalysts have been prepared conventionally by reducing Pt and M precursors in solution stepwise or simultaneously, typically at high M content, e.g., Pt/Co = 2/3. Then, the excess M atoms are leached out by acid treatment, resulting in skeleton-like Pt deposition, followed by annealing in order to form a Pt-skin layer on the alloy particles.\(^{16-18}\) However, the catalyst particle size and their alloy composition are not uniform, as depicted in Figure 1A, and therefore the thickness of deposited Pt-skeleton and the resulting Pt-skin should not be equivalent, leading to lower than expected MA and durability. Here, we propose a new concept for Pt-M alloy catalysts consisting of nearly pure nonprecious-metal M cores covered with targeted numbers of Pt-skin layers. If such a structure can be successfully prepared, as we show in the present work, and the core-induced modification of the electronic structure of the Pt-skin, as well as its durability, can still be retained under practical operating conditions, it will be possible to achieve significant reduction of the Pt loading in FCVs and other applications. The first step in our procedure shown in Figure 1B is the hydrogen heat-treatment (HHT) of the alloy core particles to induce an exchange of Pt in the interior of the particle to the surface of the nanoparticles, so that the non-noble core metal is protected during the subsequent step. The number of Pt-skin layers on the alloy nanoparticles resulting from the Pt segregation is dependent on the alloy composition and the particle size. Figure 2 shows numbers of Pt-skin layers calculated as a function of the particle sizes of Pt\(_3\)Co, PtCo and PtCo\(_3\) alloys, assuming that these particles have a cuboctahedral shape, as reported previously,\(^ {21}\) and that 100% of the Pt from the bulk of each particle segregates to the surface as a result of the heat-treatment in H\(_2\) atmosphere. The dashed line indicates one atomic layer (1AL) level of Pt-skin formation, which intersects the Pt\(_3\)Co and PtCo lines at 1.2 and 2.2 nm, respectively, indicating the minimum particle size necessary to obtain a pure Co core covered with 1 AL Pt-skin. For larger particles, the surfaces can in principle be covered with more than 1 AL Pt, Figure 2 also indicates that, for high Co content alloys such as PtCo\(_3\), it may not be possible to form a complete Pt-skin layer for \(d < 4\) nm. However, PtCo alloy particles with \(d \geq 2.2\) nm contain sufficient Pt to be covered with a complete atomic Pt layer, so that we can expect there to be no dissolution of Co, as well as Pt, during the subsequent process of Pt-skin layer formation. This feature, indicated in Figure 2, provides an extremely important advantage of the proposed method here compared to previously reported methods,\(^ {14-18}\) because we are able to precisely control the particle size and chemical composition of the core alloy, so that we can obtain a catalyst with a designed size and composition in a simple procedure, with uniform coverage of the Pt-skin layers, without losing any alloy components from the core alloy nanoparticles. In methods such as the galvanic replacement of CuUPD with a Pt monolayer proposed by Adzic and Cochell,\(^ {14,15}\) even though this approach would lead to the maximum utilization of Pt, it may be difficult to uniformly cover the core particles with the Pt-skin, since only a single Pt-skin layer is used, resulting in a probable dissolution of core components such as Pd, and the possible need to deposit additional Pt layers by repeating the process.

Experimental

Preparation of core alloy catalysts supported on GCB for additional Pt-skin formation.—To begin the preparation of the new type of Pt-skin catalysts proposed in this paper, uniformly dispersed PtCo (1:1 atomic ratio) alloy nanoparticles on the GCB support
(150 m² g⁻¹), denoted as “PtCo/GCB”, (20 wt% loading of metal catalyst with a mean particle size, d, of ca. 2.5 nm, as shown in Table I and II) were prepared, based on the design concept and discussion mentioned above, by the nanocapsule method (with heat-treatment at 400°C in N₂ atmosphere for 4 h at the final preparation stage to stabilize the alloy and to remove the remaining surfactant).¹⁹,²⁰ These particles were then used as a base for further deposition. Prior to the deposition of the Pt-skin, the PtCo/GCB powder was heat-treated in 5% H₂ atmosphere (N₂ balance) at 200°C for 30 min to segregate the Pt atoms to the surface from the interiors of the PtCo particles (Figure 2), which is supported by the experimental evidence presented in the following section. One can expect that at least one atomic layer of Pt-skin was formed on the surfaces of the PtCo alloy particles (with the composition of Pt/Co ≥ 1/1) as a result of this treatment (see Figure 2), which is supported by the experimental evidence presented below. Hereinafter, we denote the PtCo/GCB heat-treated in 5% H₂ at 200°C as “Pt¹×AL-PtCoHT(2)/GCB,” for which the atomic fraction of Co in the particle interior has increased due to the enrichment of Pt atoms on the surface. In addition, we examined the feasibility of further simplification of the two-step heat treatments described above by means of a one-step treatment in 5% H₂ at 400°C for 4 h, denoted as “Pt¹×AL-PtCoHT(4)/GCB,” from the viewpoint of the controllability of the particle size and Pt-skin formation. If Pt atoms had not been segregated on the surface by the above treatment, Co atoms would have been exposed and would have easily dissolved into the acidic solution formed in the process of the deposition of the additional atomic Pt layer at the present work, or into the acidic electrolyte used as described in our previous work on sputtered PtCo and PtFe alloy films, based on XPS, STM and EQCM analyses (e.g., Refs. 4–6). The achievement of Pt surface segregation was strongly supported by the complete lack of solution-phase Co due to dissolution from the alloy particles during the additional Pt layer formation process, as described in the following section.

*Formation of Pt-skin with targeted thickness on core alloy catalyst surfaces.*—The preparation of the catalyst with an additional one atomic layer Pt-skin, for example, on Pt¹×AL-PtCoHT(2)/GCB as was carried out as follows. The Pt¹×AL-PtCoHT(2)/GCB powder (50 mg, for example) was dispersed in ultrapure water, boiled for 30 min, and then cooled to 60°C. After addition of hydrogen hexachloroplatinate (IV) hexahydrate (H₂PtCl₆·6H₂O) solution, 5% H₂ gas was sparged during vigorous stirring with a mechanical homogenizer for 1 h to form the additional 1AL Pt-skin on the core particles. Amounts of the precursor required for the 1AL Pt-skin were calculated by use of the experimental evidence that were derived assuming a cuboctahedral shape, which seemed to be reasonable from the observation of single crystalline Pt-skin catalyst particles with a predominance of (111) facets, with some (100) facets, in high-angle annular dark-field (HAADF)-STEM images, as shown in Figure 5 and in our previous work.²¹ The pH value of the solution was an important factor for the Pt-skin formation, with the effect on the reduction level to metallic Pt particles presented in the Supporting Information (Figure S1). The percentage conversion to Pt-skin by H₂ sparging for 1 h exhibited higher values at higher pH values and levelled off at approximately 100% at pH ≥ 1.5. In this research, therefore, the skin formation was performed at pH ≥ 2.0 by preparing the mixed core-catalyst/Pt-precursor suspension in pure water, with the respective amounts being estimated in such a way that the final pH would be greater than 2.0 when the Pt deposition was complete, without the addition of base. Finally, this mixed solution was filtered and washed with ultrapure water. The Pt-skin modified Pt¹×AL-PtCoHT(2)/GCB powder prepared in this way was dried in vacuum at 60°C. Neither Pt nor Co was detected in the filtrates by use of inductively coupled plasma mass spectroscopy (ICP-MS), indicating that the entire amount of Pt precursor was deposited on the core particle surfaces by the reduction with H₂, and the Co remained in the interior. The enriched Pt layer on the Pt¹×AL-PtCoHT(2) particles in the intermediate stage was able to effectively suppress the dissolution of the underlying Co-enriched core during the subsequent Pt-skin formation process. If this had not been the case, Co atoms existing in the surface layers would have dissolved, as found in our previous work.²¹⁻⁶ This fact was also confirmed by the ICP-MS analysis of Pt and Co contents in the final product, being reasonably well consistent with

### Table I. Properties of as-prepared PtCo/GCB and Pt¹×AL-PtCoHT(4)/GCB catalysts.

| Core metal             | Projected values ¹⁺) | Measured values          |
|------------------------|-----------------------|--------------------------|
|                        | X (nm) | d (nm) | Metal loaded (wt%) | Overall Pt (atom %) | dTEM (nm) | d⁰ (nm) ²⁺) | dKRR (nm) | dSCA (nm) | Metal loaded (wt%) | Overall Pt (atom %) |
| Pt¹×AL-PtCoHT(4)       |         |        |                  |                        |          |            |            |            |                        |                      |
| X = 0                  | 2.5     | 2.7    | 20.0             | 50                     | 2.5 ± 0.2 | 2.5        | 2.4        | 2.5        | 50                     | 2.4                  |
| X = 1                  | 3.0     | 3.8    | 29.1             | 65                     | 2.5 ± 0.2 | 2.5        | 2.3        | 2.6        | 65                     | 2.6                  |
| X = 2                  | 4.0     | 6.8    | 47.1             | 75                     | 3.0 ± 0.3 | 3.1        | 2.8        | 2.9        | 75                     | 2.9                  |

¹⁺) Projected values for the Pt¹×AL-PtCoHT(4)/GCB catalysts with additional Pt-skin layer number(s), X. Prepared by the H₂ reduction process: (i) mean particle sizes (d), (ii) loaded metal amounts (wt%) and (iii) overall Pt content (atom %), which were calculated based on the as-prepared PtCo/GCB with dTEM = 2.5 ± 0.2 and the metal loading of 27.2 wt% on GCB, assuming all of the catalyst particles to have a cuboctahedral structure.

²⁺) The average particle size d⁰ based on the particle surface area was calculated by the same manner as those of Table I.

### Table II. Properties of Pt¹×AL-PtCoHT(2)/GCB catalysts.

| Core metal             | Projected values ¹) | Measured values          |
|------------------------|---------------------|--------------------------|
|                        | X (nm) | d (nm) | Metal loaded (wt%) | Overall Pt (atom %) | dTEM (nm) | d⁰ (nm) ²) | dKRR (nm) | dSCA (nm) | Metal loaded (wt%) | Overall Pt (atom %) |
| Pt¹×AL-PtCoHT(2)       |         |        |                  |                        |          |            |            |            |                        |                      |
| X = 0                  | 2.5     | 2.0    | 20.0             | 50                     | 2.6 ± 0.2 | 2.6        | 2.6        | 18.7       | 49                     |
| X = 1                  | 3.0     | 2.9    | 29.1             | 65                     | 2.9 ± 0.2 | 2.9        | 3.3        | 29.0       | 66                     |
| X = 2                  | 4.0     | 4.7    | 47.1             | 75                     | 3.6 ± 0.3 | 3.6        | 3.7        | 47.5       | 75                     |
| X = 3                  | 5.0     | 6.8    | 68.5             | 82                     | 4.3 ± 0.4 | 4.4        | 4.5        | 65.0       | 83                     |

¹) Projected values for the Pt¹×AL-PtCoHT(2)/GCB catalysts with additional Pt-skin layer number(s), X. Prepared by the same manner as the Pt¹×AL-PtCoHT(2)/GCB catalyst: (i) mean particle sizes (d), (ii) loaded metal amounts (wt%) and (iii) overall Pt content (atom %), which were calculated based on the as-prepared PtCo/GCB with dTEM = 2.5 ± 0.2 and the metal loading of 20 wt% on GCB, prepared as a new batch, separate from that of Table I.

²) The average particle size d⁰ based on the particle surface area was calculated by the same manner as those of Table I.
both the targeted and measured values for the loaded metal amounts or overall Pt contents after the additional Pt-skin formation from 1 AL to 4 AL, (see Table II). The catalyst thus formed, with one additional atomic skin-layer, will be denoted as $\text{Pt}_{\text{AL}}$-$\text{PtCoHT(2)}$-GCB. Any number of Pt-skin layers discussed in this paper can be deposited simply by dissolving the amounts of Pt precursor equivalent to the targeted thickness in the above process. A possible mechanism for the present atomically tuned Pt-skin formation on nano-sized core catalysts is discussed in terms of a model surface similar to that of $\text{Pt}_{\text{AL}}$-$\text{PtCoHT(2)}$ as an example in the Supporting Information (see Figure S5).

**Stabilization of the Pt-skin formed by the post heat-treatment in $\text{H}_2$—**We heat-treated the above catalysts additionally in 5% $\text{H}_2$ atmosphere ($\text{N}_2$ balance) at 200°C for 30 min and examined the effect of the treatment on the activity and stability for the ORR at 65°C in 0.1 M $\text{HClO}_4$.

**Evaluation of the size-distribution and elemental-distribution of Pt-Co catalysts on the GCB support with TEM.**—In order to clearly confirm the formation of the appropriate thickness and morphology of the Pt-skin layers on every core-alloy particle surface, we observed the supported catalysts before/after the Pt-skin formation with spherical aberration (SA)-corrected scanning transmission electron microscopy, STEM (Hitachi HD-2700, EV = 200 and 80 kV) with EDX, (Bruker Quantax XFlash 5030). About 500 catalyst particles observed in transmission electron microscopy, TEM, (Hitachi H-9500, acceleration voltage = 200 kV) images were used to obtain the particle size distribution and the average particle diameter ($d_{\text{TEM}}$), which were compared with the results obtained by the conventional X-ray diffraction (XRD) and electrochemical cyclic voltammogram (CV) methods, explained below. The overall Pt content shown in Table II was determined as an average of 20 randomly selected catalyst particles with EDX analysis of the TEM images. Line scan EDX analysis was also performed on single catalyst particles after the three stages of Pt-skin formation.

**Electrochemical measurements.**—In order to obtain the pure kinetically controlled currents, avoiding mass transport limitations, the test catalysts were uniformly dispersed at a low constant loading of carbon support, 11.0 $\mu$g cm$^{-2}$ on an Au substrate (geometric area 0.04 cm$^2$), then coated with Nafion solution (thickness 0.1 mm), and evaluated for their performance by the multi-channel flow double electrode cell (M-CFDE) technique, where electrode flow rate $U_f$ (measured by means of a potential scan at 1 mV s$^{-1}$) for the former and 0.5 V s$^{-1}$ for the latter, in N$_2$-saturated 0.1 M $\text{HClO}_4$ solution at 65°C. These electrochemical measurements were repeated after given numbers of potential cycling sets for both durability tests up to 30,000 or 50,000 total cycles.

**Results and Discussion**

**Effects of the pre-heat-treatment for Pt segregation on the particle-size distribution and the additional Pt-skin formation.**—Figures 3A and 3B show X-ray diffraction (XRD) and lattice constants, respectively, for PtCo/GCB, Pt$_{\text{AL}}$-$\text{PtCoHT(4)}$-GCB, and Pt$_{\text{AL}}$-$\text{PtCoHT(2)}$-GCB, as an example. It was found that all of the diffraction peaks for PtCo/GCB and Pt$_{\text{AL}}$-$\text{PtCoHT(4)}$-GCB shifted to higher angles than those corresponding to the pure face-centered cubic structure (fcc) Pt structure, indicatingfcc solid-solution-type alloy formation, with no detectable peaks corresponding to the face-centered tetragonal (fct) ordered-alloy structure, as seen in our previous work. The lattice constant calculated for the PtCo/GCB and Pt$_{\text{AL}}$-$\text{PtCoHT(4)}$-GCB catalysts were consistent with a linear correlation between the lattice constants and Co content for a series of our Pt-Co alloys with different compositions. In contrast, the Pt$_{\text{AL}}$-$\text{PtCoHT(2)}$-GCB exhibited split diffraction peaks, i.e., new peaks at smaller angles close to those of pure Pt, in addition to the original peaks for Pt$_{\text{AL}}$-$\text{PtCoHT(4)}$-GCB, as a shoulder on the former, in agreement with the XRD results observed for the corrosion process for PtCo/CB and for the 2n-Pt MAL–PtCo/CB reported earlier. This result is one of the pieces of evidence supporting the Pt-skin formation on the core particle surfaces.

The mean crystallite sizes ($d_{\text{CRYS}}$) of various catalyst particles were evaluated by applying the Scherer equation for the XRD peak assigned to the (220) plane at $2\theta = 67^\circ$, which are shown in Table I. We calculated the average particle diameters ($d_{\text{TEM}}$ and $d_{\text{TEM}}$) based on the numbers and surface areas, respectively, of particles observed with TEM and have included them in Tables I and II. However, the two sets of values showed no noticeable differences, probably due to the distinctively sharp size distribution of the catalysts prepared by the nanocapsule method. Hereinafter, for brevity, the former values will be used for the discussion. The mean particle sizes ($d_{\text{ECSA}}$) were evaluated by use of ECSA measurements, referring to Figures S3 and S4, based on the initial (N=0) CV results for hydrogen adsorption, as widely accepted for Pt-based catalysts and also shown in Table I. The mean particle size estimates of PtCo/GCB, heat-treated (HT) in N$_2$ at 400°C, were 2.5 ± 0.2 nm ($d_{\text{TEM}}$), 2.4 nm ($d_{\text{CRYS}}$) and 2.5 nm ($d_{\text{ECSA}}$). The particle size of Pt$_{\text{AL}}$-$\text{PtCoHT(4)}$-GCB, one-step HT (5% $\text{H}_2$ at 400°C), was nearly the same: 2.5 ± 0.2 nm ($d_{\text{TEM}}$), 2.3 nm ($d_{\text{CRYS}}$) and 2.6 nm ($d_{\text{ECSA}}$). The results clearly show that the applied H$_2$ treatment, carried out with the objective of segregating the Pt atoms from the alloy cores to the surfaces, caused noticeable...
particle aggregation. From this result, it is clear that the Pt segregation induced by the two-step heat-treatment (N\textsubscript{2} at 400 °C followed by 5% H\textsubscript{2} at 200 °C) for the Pt\textsubscript{1AL-PtCoHT(4)}/GCB did not lead to discernible particle growth.

After one additional Pt-skin was deposited on the Pt\textsubscript{1AL-PtCoHT(2)}/GCB, the average particle sizes determined for Pt\textsubscript{1AL-PtCoHT(4)}/GCB were 3.0 ± 0.3 nm (d\textsubscript{TEM}), 2.8 nm (d\textsubscript{XRD}) and 2.9 nm (d\textsubscript{ECSA}). Thus, the increase in the particle sizes resulting from the Pt deposition on the core catalyst coincided well with each other, i.e., ca. 0.5 nm, irrespective of the evaluation method. This value corresponds to a Pt-skin thickness of one atomic layer, assuming that the deposition was uniform on each particle surface. After the formation of the targeted single atomic layer of Pt-skin on the Pt\textsubscript{1AL-PtCoHT(4)}/GCB, the particle size was found to increase from 2.6 ± 0.2 nm (d\textsubscript{TEM}) and 2.6 nm (d\textsubscript{ECSA}) to 2.9 ± 0.2 nm (d\textsubscript{TEM}) and 3.3 nm (d\textsubscript{ECSA}), i.e., 0.3–0.7 nm, which indicates approximately 1 AL Pt-skin formation. After the formation of the targeted single atomic layer of Pt-skin on the Pt\textsubscript{1AL-PtCoHT(4)}/GCB, the particle size was found to increase from 2.6 ± 0.2 nm (d\textsubscript{TEM}) and 2.6 nm (d\textsubscript{ECSA}) to 2.9 ± 0.2 nm (d\textsubscript{TEM}) and 3.3 nm (d\textsubscript{ECSA}), i.e., 0.3–0.7 nm, which indicates approximately 1 AL Pt-skin formation. After the formation of the targeted single atomic layer of Pt-skin on the Pt\textsubscript{1AL-PtCoHT(4)}/GCB, the particle size was found to increase from 2.6 ± 0.2 nm (d\textsubscript{TEM}) and 2.6 nm (d\textsubscript{ECSA}) to 2.9 ± 0.2 nm (d\textsubscript{TEM}) and 3.3 nm (d\textsubscript{ECSA}), i.e., 0.3–0.7 nm, which indicates approximately 1 AL Pt-skin formation. After the formation of the targeted single atomic layer of Pt-skin on the Pt\textsubscript{1AL-PtCoHT(4)}/GCB, the particle size was found to increase from 2.6 ± 0.2 nm (d\textsubscript{TEM}) and 2.6 nm (d\textsubscript{ECSA}) to 2.9 ± 0.2 nm (d\textsubscript{TEM}) and 3.3 nm (d\textsubscript{ECSA}), i.e., 0.3–0.7 nm, which indicates approximately 1 AL Pt-skin formation.
in these images are shown in Figures 5D, 5E, 5F. Because most of the catalyst particles at all three stages displayed clear lattice and atomic images, as well as facets consisting mainly of (111) planes, it is reasonable to consider that the particles were single crystallites. For the PtCo particles in Figure 5D, the concentration distributions of both Pt and Co were fairly uniform among the particles, reflecting a random distribution of Pt and Co atoms in the solid-solution (disordered) alloy. However, the Pt2AL-PtCoHT(4) nanoparticles exhibited a higher concentration of Pt than Co from the center to the edge and a Pt distribution ca. 0.5 nm wider than that of Co, with clear edges of the grown facets, as shown in Figure 5F. The distribution of both elements in Pt1AL-PtCoHT(4) nanoparticles appeared to be midway between those of as-prepared PtCo and Pt3AL-PtCoHT(4). These observations provide clear evidence for Pt-skin formation with uniform thickness on the core Pt1AL-PtCoHT(4) particles.

**Effects of the thickness of Pt-skin layers and their annealing by post-heat-treatment on MAk and durability.**—Pt1+XAL-PtCoHT(2)/GCB catalysts (X = 0, 1, 2, 3) were prepared by the method mentioned above, for which the histograms and properties are shown in Figure 6B and Table II, respectively. All of the catalysts, with different targeted Pt-skin numbers, exhibited a sharp particle size distribution and appropriate increase in particle size, i.e., approximately 0.5 nm, corresponding to 1 AL Pt-skin thickness, resulting in average particle sizes of 2.6 ± 0.2, 2.9 ± 0.2, 3.6 ± 0.3 and 4.3 ± 0.4 nm. Both the targeted and experimentally analyzed increases in metal loading amount on the GCB support and the overall Pt content in the particles were quite consistent with each other, as shown in Table II. These results show the successful formation of Pt-skin layers from 1 AL to 4 AL on average, on the core Pt1AL-PtCoHT(2)/GCB surface. Figure 6A shows the corresponding MAk values as a function of the potential cycle numbers (N) for the load-cycle durability test. The initial MAk for X = 0, the core Pt1AL-PtCoHT(2)/GCB, exhibited the highest value, and those for the different X values decreased in order from 0 to 3, which were, however, still 2.4, 2.2, 1.7 and 1.1-fold higher than that of the commercial catalyst c-Pt/CB (TEC10E50E, Tanaka Kikinzoku Kogyo) shown in Figure 9A. After N = 30,000, it was found that their MAk values were maintained at 32, 47, 21 and 18%, respectively, compared to the initial values. These results indicate that the 2AL Pt-skin catalyst is preferable from the viewpoints of both activity and durability.

Figure 7 shows the effect of post-heat-treatment of the Pt1+XAL-PtCoHT(2)/GCB catalysts (X = 1, 2, 3) in 5% H2 atmosphere after Pt-skin formation on the initial MAk values and their load-cycle durability.
The initial $MA_k$ for $X = 1$, i.e., 2 AL Pt-skin layers, was the highest, and the values decreased in order from 2 to 3, showing further increases from those of the original values shown in Figure 6, i.e., 2.2-fold increasing to 2.5-fold, 1.7-fold increasing to 2.2-fold, and 1.1-fold increasing to 1.5-fold, respectively, in comparison with that of c-Pt/CB shown in Figure 9A. After $N = 30,000$, it was also found that the remaining levels of these $MA_k$ values were improved noticeably as a result of the post-heat-treatment, i.e., 47% increasing to 68%, 21% to 30%, 18% to 22%, respectively. The observed distinctive effect can be explained as an annealing effect, which would have reduced any defective portions of Pt-deposition into a smooth layer, as depicted by the inset in Figure 5. These results indicate that the 3 AL or 4 AL Pt-skin layers were too thick to be modified electronically by the underlying Co-enriched core.

**Effect of the core alloy composition on the $MA_k$ and the durability.**—In addition, we prepared Pt-skin layer on a Pt$_3$Co core alloy in the same manner described above. The core Pt$_3$Co/GCB with mean particle size of ca. 2.5 nm, similar to that of PtCo/GCB, was heat-treated in 5% H$_2$ for the Pt segregation (step 1), followed by an additional deposition of 1 AL Pt-skin and annealing in 0.5% H$_2$ atmosphere (step 2). As a result of step 1 for the segregation, we can expect to obtain a range of surface composition from at least 1 AL Pt-skin formation, leaving some Pt atoms in the alloy interior, up to 2 AL Pt-skin, if all of the Pt atoms became segregated perfectly on the surfaces of the particles, as shown in Figure 2. As a result of step 2 for the additional 1 AL Pt-skin deposition, therefore, the final catalyst particles may be covered by 2 to 3 ALs of Pt-skin, as depicted in Figure 8, with the schematic structure models corresponding to both extremes. Although we did not evaluate the Pt-skin thickness experimentally, for convenience, the catalyst obtained is denoted as Pt$_{2n}$Al-Pt$_2$Co$_{n+1}$HT(2)/GCB*, which has approximately the same mean particle diameter as Pt$_{2n}$Al-Pt$_3$Co$_{n+1}$HT(2)/GCB, i.e., ca. 3 nm. The former, however, has a thicker Pt-skin layer, i.e., 2–3 ALs, and smaller total Co atomic contents, i.e., 33%, compared to values of 2 ALs and 50% Co for the latter.

Figure 8 shows the effect of the composition of the core alloy upon the $MA_k$ and durability of each catalyst covered with an additional 1 AL Pt-skin layer. The initial $MA_k$ for the Pt$_3$Al-Pt$_3$Co$_{3+1}$HT(2)/GCB* was lower than that for Pt$_{2n}$Al-Pt$_2$Co$_{n+1}$HT(2)/GCB, i.e., 1.7-fold vs. 2.5-fold higher, respectively, than that for c-Pt/CB shown in Figure 9A. Assuming that both catalysts were covered with 2 AL skin layers, we can judge that the lower Co content in the interior core leads to a lower enhancement for the ORR. On the other hand, for 3 AL skin layers, it can be assumed that the inferior performance of Pt$_{2n}$Al-Pt$_3$Co$_{n+1}$HT(2)/GCB* may be attributed to the thicker Pt-skin layers, resulting from

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**Figure 8.** Effect of the gross composition of Nafion-coated catalyst particles on the $MA_k$ for the ORR at 0.85 V as a function of $N$ in the load-cycling durability test; (red) PtCo = 1/1 and (blue) PtCo = 3/1. Measurements of the activities were performed in O$_2$-saturated 0.1 M HClO$_4$ solution at 65°C.

**Figure 9.** Plots of (A,C) $MA_k$, and (B,D) $j_k$, for the ORR at Nafion-coated (red) Pt$_{2n}$Al-Pt$_2$Co$_{n+1}$HT(2)/GCB, (blue) 2n-Pt$_{2n}$Al-PtCo/GCB, (green) PtCo/GCB, and (black) c-Pt/CB electrodes at 0.85 V as a function of $N$ in the durability tests protocols for load-change cycles (A,B) and for start-stop cycles (C,D) at 65°C in N$_2$-saturated 0.1 M HClO$_4$ solution. Measurements of the ORR activities between sets of durability test cycles were performed in O$_2$-saturated 0.1 M HClO$_4$ solution at 65°C.
the lower Co content in the PtCo particles, compared with PtCo particles with the same particle size of ca. 3 nm. After load-cycling of N = 30,000, it was also found that the MAk levels maintained for Pt2AL-PtCoHT(2)/GCB and Pt2AL-PtCoHT(2)/GCB were 25% and 67%, respectively. The results indicate that the durability of Pt3CoHT(2)/GCB was inferior even to that of Pt2AL-PtCoHT(2)/GCB with a larger \( d_{\text{TEM}} \) (3.6 nm) and rather similar to that of Pt2AL-PtCoHT(2)/GCB with \( d_{\text{TEM}} = 3.6 \text{ nm} \) (see Figures 7). These results indicate that the atomic ratio of Pt to the Co in the (PtCo) is one of the most important factors to achieve not only a large MAk value but also good durability. It was found in the present work that the optimum PtCo ratio, depending on the particle size, was 1/1 for the particle size \( d = 2.5 \text{ nm} \) with 2 AL Pt-skin layers. The core Co plays a role in enhancing the ORR activity and also to stabilize the surface Pt-skin layer with respect to dissolution, probably by a transfer of electron from Co to the Pt d-band, as indicated by the positive shifts of the Pt-core levels, corresponding to the d- and f-orbitals,\(^7\) i.e., the increase of Pt binding energy. The mechanistic details are under investigation with various approaches in our laboratory.

**MAk and durability of the optimized catalysts.**—Here, we report the superior ORR activity and surprising durability of Pt2AL-PtCoHT(2)/GCB, which was prepared by the newly developed method to produce an optimized structure, as described above. The results are quite distinct from those of catalysts prepared by other methods. Figures 9A shows the variations in MAk of Pt2AL-PtCoHT(2)/GCB as a function of the number of N, simulating load cycles for FCVs, in comparison with c-Pt/CB, PtCo/GCB and 2n-Pt2AL-PtCo/GCB (\( d_{\text{TEM}} = 3.0 \pm 0.4 \text{ nm} \)). All electrodes were stabilized by pre-cycling between 0.05 and 1.0 V before the durability test. The initial MAk for Pt2AL-PtCoHT(2)/GCB (1.470 A g\(^{-1}\)) was ca. 2.5-fold higher than that for c-Pt/CB (586 A g\(^{-1}\)), and approximately equal to that for PtCo/GCB and also to that for 2n-Pt2AL-PtCo/GCB. This means that the Pt-skin layer on Pt2AL-PtCoHT(2) prepared in the present research was able to benefit from the modified electronic structure by interaction with the underlying Pt2AL-PtCoHT(2) core alloy. The degradation of MAk for Pt2AL-PtCoHT(2)/GCB was suppressed noticeably, being maintained at 68% of the initial value after 30,000 cycles, whereas for c-Pt/CB declined to ca. 20% within 10,000 cycles, resulting mainly from the agglomeration of Pt particles. It is noteworthy that the MAk for PtCo/GCB decreased more steeply and approached that for c-Pt/CB after 30,000 cycles, mainly due to the de-alloying of the PtCo particles, as clarified below. The 2n-Pt2AL-PtCo/GCB exhibited a moderate degradation rate, superior to PtCo/GCB and inferior to the present Pt2AL-PtCoHT(2)/GCB.

Variations in \( j_k \) for these catalysts as a function of N, simulating start-stop cycles for FCVs, are shown in Figure 9B. The \( j_k \) value for c-Pt/CB was nearly unchanged, which is reasonable, since the value based on the ECSA should be independent of particle agglomeration. However, the \( j_k \) values for PtCo/GCB as well as 2n-Pt2AL-PtCo/GCB decreased steeply with increasing N; in particular, the former approached a value identical with that for c-Pt/CB beyond 30,000 cycles, suggesting that defective Pt-skin layers were formed on both catalysts, which were unable to suppress the dissolution of Co during cycling. In contrast, it was found that \( j_k \) for Pt2AL-PtCoHT(2)/GCB was maintained at a high, constant value to 30,000 cycles. This clearly indicates that the Pt-skin layers prepared by the present preparation method protected the core perfectly from the dissolution of Co, so that \( j_k \), which was based on the ECSA value, was maintained constant, even though particle agglomeration occurred, as indicated by a slow decrease in MAk with increasing N.

Figure 9C shows the variations in MAk for these catalysts as a function of N for the potential sweep protocol simulating start-stop cycles for FCVs. The degradation of MAk for the Pt2AL-PtCoHT(2)/GCB catalyst was suppressed to a greater extent than that observed during the load-cycling test, and MAk was maintained at 75% of the initial value after 30,000 cycles, while those for PtCo/GCB and 2n-Pt2AL-PtCo/GCB decreased steeply to ca. 60% of the initial value. It is especially noteworthy that the \( j_k \) value for Pt2AL-PtCoHT(2)/GCB was maintained at 93% of the initial value, even after 30,000 cycles (Figure 9D). Such a suppression of the de-alloying at high potentials (1.0 → 1.5 V) is one of the surprising properties of Pt2AL-PtCoHT(2)/GCB, since the de-alloying of conventional alloy catalysts such as PtCo/GCB is typically accelerated during cycling at high potentials.

Regarding studies of the activity and durability of similar Pt-based alloy catalysts in HClO\(_4\) solution available in the literature (refer to Table S1), one in particular was considered useful as a benchmark,\(^{16}\) even though the catalyst was different and the test conditions and protocols were slightly different from those used here. In that work, an optimized catalyst, Pt-PtNi, with a thin Pt film \((<3 \text{ ML})\), exhibited an improvement factor of ca. 2.5 compared with a polycrystalline Pt surface, and an acid-treated, annealed PtNi nanoparticle catalyst on CB exhibited improvement factors of ca. 6.5 compared with Pt/CB in terms of both surface area and mass, with an initial surface-specific activity of ca. 0.95 mA cm\(^{-2}\) (Pt) obtained by the CV at 20 mV s\(^{-1}\), prior to potential cycling, compared with our values of ca. 0.25 to 0.3 mA cm\(^{-2}\) for Pt2AL-PtCoHT(2)/GCB obtained under quasi-steady state by the CV at 0.5 mV s\(^{-1}\) (Pt) (Fig. S6(B)). This difference is most likely due to the higher intrinsic activity of Pt-Ni catalysts, as we have also found in work that will be reported separately. However, as shown in Fig. S7(A) for mass activity and Fig. S7(B) for surface-specific activity, the durability of the present catalyst is extremely encouraging and is superior to that reported for the acid-treated, annealed catalyst. The retention of MAk for our Pt2AL-PtCoHT(2) catalyst was 99% and that for \( j_k \) was 100% after 5,000 load-change cycles (Fig. S7(A)), compared to values of 74% and 85%, respectively, after 4,000 cycles in the work cited.\(^{16}\) Even more striking is the retention of activity after 30,000 potential cycles, as already noted above and shown for the industry-standard 0.9 V in Fig. S6.

**Summary**

We have succeeded in preparing Pt-skin layers on Co-enriched alloy core-surfaces minimizing Pt content in a simple, precisely controllable fashion and demonstrated clearly the importance of the uniform 2 AL Pt-skin formation on their surfaces, which we expect will lead to superior stability in practical FCV applications; this method could, in principle, be applied to other catalyst systems.

We emphasize that, in contrast to previously reported approaches, that introduced here resulted in a narrow distribution of size and composition, with highly uniform Pt skin layers, ideally two, on highly Co-enriched cores, so that the electronic properties of the surface were still influenced by those of the core. Thus, we propose that the present approach should combine near-ideal simplicity with optimized ORR activity and durability, as well as conservation of platinum.

Detailed investigations of the ORR activity and durability of the PtCo alloy catalysts thus covered with Pt-skin, in a practical temperature range for PEFCs, and the effect of the number of Pt-skin layers and core composition are in progress in our laboratory. In addition, we are conducting a full optimization of the heat-treatment conditions for the formation of the initial Pt atomic layer.

**Acknowledgments**

This work was supported by funds for the “Research on Nanotechnology for High Performance Fuel Cells” (HiPer-FC) project and “Superlative, Stable, and Scalable Performance Fuel Cell” (S-Per-FC) project from the New Energy and Industrial Technology Development Organization (NEDO) of Japan. The authors thank M. Kodama for her contribution to the TEM observations.

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