Oxygen Reduction Reaction Activity of Carbon-Supported Pt-Fe, Pt-Co, and Pt-Ni Alloys with Stabilized Pt-Skin Layers

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ABSTRACT

We have prepared carbon-supported Pt-M (M = Fe, Co, and Ni) alloy nanoparticles with uniform size and composition as cathode catalysts for polymer electrolyte fuel cells. In order to protect the underlying Pt-M alloy from dealloying and maintain high mass activity for the oxygen reduction reaction (ORR), two atomic layers of Pt-skin (Pt2AL) were formed on the Pt-M nanoparticles. By means of various types of analysis, including X-ray diffraction (XRD), inductively coupled plasma mass analysis (ICP-MS), thermogravimetry (TG), and transmission electron microscopy (TEM), the formation of monodisperse Pt2AL-Pt-M/C was confirmed. The kinetically-controlled ORR activities (mass activity, MA, and area-specific activity, jk) for the ORR at Nafton®-coated Pt2AL-Pt-M/C catalysts in O2-saturated 0.1 M HClO4 solution were evaluated by the use of a multi-channel flow double electrode cell at 65°C. It was found that the initial value of MA of Pt2AL-PtNi/C was the highest, i.e., 3.3 times higher than that at a commercial catalyst, carbon-supported Pt (c-Pt/C). In contrast, the Pt2AL-PtCo/C catalyst exhibited superior durability, so that dealloying was almost entirely suppressed, together with a great mitigation of the particle agglomeration after applying 10^4 cycles of potential steps between 0.6 V and 1.0 V.

Keywords : Polymer Electrolyte Fuel Cell, Electrocatalyst, Pt alloy, Oxygen Reduction Reaction

1. Introduction

Polymer electrolyte fuel cells (PEFCs) have been developed specifically for clean and energy-efficient applications such as residential co-generation systems and fuel cells vehicles (FCVs). Since the first commercialization of a 1 kW-class residential PEFC (ENE-FARM® system in 2009 in Japan, the cumulative number of systems installed has exceeded 120,000 in fiscal year 2014. The Toyota Motor Corporation commenced to sell a FCV called the “MIRAI” in December, 2014. Costly Pt-based cathode catalysts have been employed for the oxygen reduction reaction (ORR): O2 + 4H+ + 4e− → 2H2O in the strongly acidic environment of PEFCs operated at low temperature (below 100°C). To increase the mass activity MA (A gPt⁻¹) for the ORR, which is defined as the product of the area-specific activity jk (ORR current density per active surface area, A m⁻²) and the electrochemically active area ECA (m² gPt⁻¹), Pt-based nanoparticles have been supported on high-surface-area carbon black.

As the result of an extensive research and development (R & D) program involving the catalyst itself and its effective utilization in the cathode catalyst layers (CLs), the Pt loading in the CLs has been reduced remarkably. However, to promote large-scale commercialization, it is essential to further reduce the amount of Pt, by increasing both the MA and the durability of the catalyst. The use of Pt alloyed with nonprecious metals such as Cr, Fe, Co, Ni, Cu, etc. has been recognized to be very effective in increasing jk values.3,4 By using multiple types of analyses,5,6 we clearly demonstrated that nonprecious metal elements in Pt-M (M = Fe, Co, Ni) solid solutions were leached out in an acidic electrolyte, but a Pt-skin layer was spontaneously formed on the alloy surface. The Pt-skin layer protected the underlying alloy from corrosion, and its electronic state modified by the alloy induced the enhanced jk values.

In spite of considerable R & D on Pt alloy nanocatalysts, the optimum chemical composition and particle size, having both high MA and high durability, are still unclear. One of the major reasons is that the conventional preparation methods4-8 of such alloy nanoparticles have provided inhomogeneous composition with a broad size distribution, resulting in the formation of non-uniform Pt-skin layers. We have developed the nanocapsule method to prepare monodisperse Pt alloy nanoparticles uniformly dispersed on carbon supports with well-controlled composition.9,10 For example, the kinetically-controlled mass activity MA of a carbon-supported PtCo (atomic ratio) catalyst at 30 to 70°C was found to be 3.3 times higher than that of commercial carbon-supported Pt catalyst (c-Pt/C).11 However, the durability of our Pt3Co/C catalyst was insufficient, since the dealloying of Co was not fully suppressed at high temperatures > 80°C, with the catalyst gradually becoming deactivated so that the MA value was finally comparable to that of c-Pt/C. Besides the degradation of the catalytic activity, the accompanying dissolution of nonprecious metal components must be avoided, because protons in the polymer electrolyte membrane and the electrolyte binder (ionomer) in the CL could be easily exchanged with the metal cations, inducing two types of serious damage as follows. First, the contamination by the metal cations leads to decreases in the proton conductivity, oxygen solubility, and oxygen diffusion rate, resulting in a decreased ORR rate.12,13 Second, some metal cations (specifically, Fe3+ and Cu2+) accelerate the formation of OH radicals from H2O2, which can degrade the polymer electrolyte and the gasket material;14,15 H2O2 is generated both via the two electron-reduction of O2 (side reaction) at the cathode and via the reaction of crossover O2 (through the membrane) with H2 adsorbed at the anode. To mitigate the latter damage, the H2O2 yield (the percentage of H2O2 production rate with respect to that of the overall ORR) of the catalyst should be as low as possible.
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By using a stepwise nanocapsule method, we have succeeded in preparing a thin, stable Pt-skinned layer on Pt-Co alloy nanoparticles, which were dispersed on graphitized carbon black (GCB). The average thickness of the stabilized Pt-skinned corresponded to two atomic layers, but a small fraction (ca. 4 vol.%) of pure Pt nanoparticles (ca. 1.5 nm) was also deposited on the GCB. The dealloying of Co was found to be suppressed, with high values of M\(_{50}\) being maintained even at 90°C. This catalyst also exhibited much lower \(\text{H}_{2}\text{O}_2\) yield than that of c-Pt/C at all temperatures examined. Very recently, we have developed a facile preparation method of the stabilized Pt-skinned layers on supported nanocatalysts. It was found that PtCo alloy with two atomic Pt-skinned layers, Pt\(_{50}\text{Al}\)-Pt/CGB thus prepared exhibited superior performances both in the \(\text{M}_{50}\) and the durability versus potential changes (simulating load-changes and start-stop cycles of FCVs), compared with those of conventional ones.

In the present research, we have examined the kinetically-controlled mass activity \(M_{50}\) and \(\text{H}_{2}\text{O}_2\) yield of Pt\(_{50}\text{Al}\)-Pt/M/C (M = Fe, Co, and Ni) in O\(_2\)-saturated 0.1 M H\(_2\text{O}_2\) solution at 65°C for the first time by the use of the multi-channel flow double electrode method. To clarify the effect of the nonprecious metal species M on the properties, Pt-M nanoparticles with uniform size were dispersed on high-surface area carbon black, followed by the formation of Pt\(_{50}\text{Al}\). It was found that the initial value of \(M_{50}\) at 0.85 V vs. RHE and 65°C increased in the order, c-Pt/C \(<\) Pt\(_{50}\text{Al}\)-Pt/C < Pt\(_{50}\text{Al}\)-Pte/C < Pt\(_{50}\text{Al}\)-PtNi/C, while the Pt\(_{50}\text{Al}\)-Pt/C catalyst exhibited superior durability to potential step cycles between 0.6 V and 1.0 V.

2. Experimental

2.1 Preparation of Pt\(_{50}\text{Al}\)-Pt/M/C Catalysts

The preparation protocol of Pt\(_{50}\text{Al}\)-Pt/M/C (M = Fe, Co, Ni) was similar to that of Pt\(_{50}\text{Al}\)-Pt/CGB, except that high-surface area carbon black (specific surface area = 780 m\(^2\)/g) was used as the support in place of GCB (specific surface area = 150 m\(^2\)/g). Here, we briefly explain the protocol. Metal acetylacetonates, Pt(acac)\(_2\), Fe(acac)\(_3\), Co(acac)\(_3\), and Ni(acac)\(_2\) were used as the precursors of the Pt-M alloys. First, Pt-M alloy (1:1 atomic ratio) nanoparticles were highly dispersed on the support (denoted as Pt-M/C) by the nanocapsule method. The projected total metal loading was 30 wt% for all samples. The Pt-M/C was heat-treated in 5% \(\text{H}_2\) (N\(_2\) balance) to segregate the Pt atoms on the surface. It was confirmed in our previous work that nearly one atomic layer of Pt-skinned (Pt\(_{50}\text{Al}\)) was formed on the surface of the Pt-Co alloy as a result of this treatment. The catalyst thus prepared will be denoted as Pt\(_{50}\text{Al}\)-Pt/M/C. Then, one more atomic layer of Pt-skinned was formed on Pt\(_{50}\text{Al}\)-Pt/M/C via controlled Pt deposition from a Pt-complex-containing aqueous solution with 5% \(\text{H}_2\) bubbling at 60°C for \(> 1\) h (until Pt-complex was reduced thoroughly), where the amount of Pt-complex required was calculated based on the average particle size of Pt\(_{50}\text{Al}\)-Pt/M/C determined among ca. 300 particles by TEM (Hitachi H-9500, operated at 200 kV). After being filtered and washed with pure water, the catalyst powder was vacuum-dried. Finally, to stabilize the Pt-skinned layer, the catalyst thus prepared was briefly heat-treated in 5% \(\text{H}_2\) at 200°C. The catalysts thus prepared will be denoted as Pt\(_{50}\text{Al}\)-Pt/M/C.

2.2 Characterization and Electrochemical Measurement of Pt\(_{50}\text{Al}\)-Pt/M/C

The Pt\(_{50}\text{Al}\)-Pt/M/C and Pt\(_{50}\text{Al}\)-Pt/M/C catalyst powders thus prepared were characterized by X-ray diffraction (XRD, Rigaku Ultima IV) with CuK\(_\alpha\) radiation (40 kV, 40 mA) and TEM. The loaded amounts of the metal catalysts on the carbon support were quantified from the weight loss by combustion of the carbon, heating to 600°C in air with the use of thermogravimetry (TG). The average compositions were quantitatively analyzed by an inductively coupled plasma mass analyzer (ICP-MS, Agilent Technologies Inc. 7500CX) after dissolving in hot aqua regia the ash remaining after the TG.

The kinetically-controlled ORR activities (\(j_k\) or \(M_{50}\)) and \(\text{H}_{2}\text{O}_2\) yield, \(P(\text{H}_2\text{O}_2)\), on three kinds of new catalysts [Pt\(_{50}\text{Al}\)-Pt/M/C (M = Fe, Co, Ni)] were evaluated under identical reaction conditions (temperature, electrolyte solution, and \(\text{O}_2\) concentration) simultaneously by the multi-channel flow double electrode (M-CFDE) technique. The working electrode was Nafion\(^a\)-coated Pt\(_{50}\text{Al}\)-Pt/M/C uniformly dispersed on an Au substrate (geometric area 0.04 cm\(^2\)), which was prepared in the similar manner as that described in our previous work. The amount of each catalyst was maintained at a constant loading of carbon support at 15 \(\mu\text{g}\text{carbon/cm}^2\) (corresponding to an approximately three-layer height of carbon particles), and the average thickness of Nafion\(^a\) was 0.1 \(\mu\)m. The ORR activities of the commercial Pt catalyst supported on carbon black (TEC10E50K, 50 wt%-Pt, specific surface area of the carbon support = ca. 800 m\(^2\)/g, Tanaka Kikinzoku Kogyo, which has been chosen as the standard catalyst) were measured separately with 5.5 \(\mu\text{g}\text{carbon/cm}^2\) (ca. monolayer height), because the dispersion state of this catalyst on the Au substrate was found to be more uniform, thus providing the intrinsic activity as described later. The reference electrode used was a reversible hydrogen electrode (RHE), and all of the potentials will be referred to the RHE in this paper.

First, all working electrodes were electrochemically stabilized by potential cycling between 0.06 and 1.00 V at 0.5 V s\(^{-1}\) in N\(_2\)-purged 0.1 M H\(_2\text{O}_2\) solution until a steady-state cyclic voltammogram (CV) was obtained. The value of \(E_C\) for each catalyst was determined from the electrical charge for the hydrogen adsorption wave in the CV measured at 0.1 V s\(^{-1}\), referred to \(\Delta Q_{\text{H}_2} = 210 \mu\text{C/cm}^2\) for bulk polycrystalline Pt. Then, hydrodynamic voltammograms were recorded by scanning the potential from 0.5 to 1.0 V for 10 min in O\(_2\)-saturated 0.1 M H\(_2\text{O}_2\) solution at 65°C. In order to detect \(\text{H}_2\text{O}_2\) generated at the working electrode, the potential of the collecting electrode was set at 1.2 V. The collection efficiency (\(\eta\)) for the collecting electrode in the present M-CFDE was experimentally determined to be 0.28 ± 0.01.

3. Results and Discussion

3.1 Characterization of Pt\(_{50}\text{Al}\)-Pt/M/C catalysts

Typical properties of synthesized Pt\(_{50}\text{Al}\)-Pt/M/C and Pt\(_{50}\text{Al}\)-Pt/M/C are summarized in Table 1. The average composition of each Pt\(_{50}\text{Al}\)-Pt/M/C analyzed by ICP-MS (Pt atom%) = 49.8% for Pt-Co, 50.8% for Pt-Ni, and 56.3% for Pt-Fe) was close to that planned for the preparation of Pt-M alloy (50.0 at%-%Pt). Figure 1 shows X-ray diffraction patterns of the Pt\(_{50}\text{Al}\)-Pt/M/C, Pt\(_{50}\text{Al}\)-Pt/M/C, and c-Pt/C catalysts. All of the diffraction peaks for c-Pt/C, as expected, were assigned to the face-centered cubic (fcc) phase of pure Pt. In contrast, the diffraction peaks for all of the Pt\(_{50}\text{Al}\)-Pt/M/C samples clearly shifted to higher angles than those of pure Pt, indicating fcc alloy formation. In contrast, the diffraction peaks for the Pt\(_{50}\text{Al}\)-Pt/M/C catalysts were observed at positions between those for the corresponding Pt\(_{50}\text{Al}\)-Pt/M/C and pure Pt. Such shifts of diffraction peaks are consistent with those reported previously. The crystallite sizes \(d_{\text{XRD}}\) of the Pt\(_{50}\text{Al}\)-Pt/M/C were calculated to be 2.2 to 2.3 nm by use of the Scherrer’s equation (see Table 1). It is noteworthy that the \(d_{\text{XRD}}\) value for each Pt\(_{50}\text{Al}\)-Pt/M/C was larger by 0.3 to 0.5 nm than that of the corresponding Pt\(_{50}\text{Al}\)-Pt/M/C.

Such increases in the particle sizes by the controlled Pt-skinned deposition were demonstrated more clearly by the TEM images. For both the Pt\(_{50}\text{Al}\)-Pt/M/C and Pt\(_{50}\text{Al}\)-Pt/M/C in Fig. 2, the catalyst nanoparticles were uniformly dispersed on the support. Based on the size distribution histogram among ca. 300 particles for each sample,
Table 1. Typical properties of synthesized Pt1AL−Pt-M/C, Pt2AL−Pt-M/C, and c-Pt/C (reference catalyst).

<table>
<thead>
<tr>
<th>M</th>
<th>Pt-skin#</th>
<th>metal loadedb (wt%)</th>
<th>compositionc (Pt atom%)</th>
<th>d_{hkl}d (nm)</th>
<th>d_{TEM}e (nm)</th>
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<tr>
<td>Fe</td>
<td>Pt1AL</td>
<td>22.0</td>
<td>56.3</td>
<td>2.2</td>
<td>2.4 ± 0.3</td>
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<td></td>
<td>Pt2AL</td>
<td>31.5 [32.3]f</td>
<td>73.1 [70.4]f</td>
<td>2.6</td>
<td>2.9 ± 0.4</td>
</tr>
<tr>
<td>Co</td>
<td>Pt1AL</td>
<td>24.4</td>
<td>49.8</td>
<td>2.3</td>
<td>2.8 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>Pt2AL</td>
<td>32.7 [34.0]f</td>
<td>67.2 [66.3]f</td>
<td>2.8</td>
<td>3.3 ± 0.5</td>
</tr>
<tr>
<td>Ni</td>
<td>Pt1AL</td>
<td>27.6</td>
<td>50.8</td>
<td>2.2</td>
<td>2.8 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>Pt2AL</td>
<td>40.8 [37.6]f</td>
<td>71.0 [64.3]f</td>
<td>2.5</td>
<td>3.2 ± 0.4</td>
</tr>
<tr>
<td>c-Pt/C</td>
<td></td>
<td>46.7</td>
<td>—</td>
<td>2.1</td>
<td>2.2 ± 0.5</td>
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#Number of Pt-skin layers formed on Pt-M alloy surface. bMetal weight percent estimated by weight loss using TG. The projected metal loading for each Pt1AL−Pt-M/C (namely Pt-M/C) catalyst was 30 wt%. cAverage composition analyzed by ICP-MS after dissolving in hot aqua regia the ash remaining after the TG. The projected alloy composition of Pt-M was 50.0 atom%Pt. dCrystal size calculated from the Sherrer’s equation for the peak assigned to (220) diffraction at 2θ ≈ 67°. eAverage particle size and standard deviation based on TEM observation. fProjected metal loading for preparing the Pt2AL−Pt-M/C catalysts. gProjected average composition calculated assuming cuboctahedrally shaped particles.10

Figure 1. X-ray diffraction patterns for Pt2AL−PtFe/C, Pt1AL−PtFe/C, Pt2AL−PtCo/C, Pt1AL−PtCo/C, Pt2AL−PtNi/C, Pt1AL−PtNi/C, and c-Pt/C. Dashed lines indicate 2θ peaks assigned to (111), (200), (220), and (311) planes (from low diffraction angle to high angle) of fcc Pt. the average particle size d_{TEM} and the standard deviation σ_{d} of the Pt1AL−PtFe/C, Pt1AL−PtCo/C, and Pt1AL−PtNi/C catalysts were 2.4 ± 0.3 nm, 2.8 ± 0.5 nm, and 2.8 ± 0.3 nm, respectively, i.e., fairly narrow particle size distributions, compared with that of c-Pt/C (σ_{d} > 20%). The size distribution histograms of all of the Pt2AL−Pt-M/C were shifted to larger size with nearly perfect maintenance of the distribution profile seen for the corresponding Pt1AL−Pt-M/C. As shown in Table 1, the increment in the d_{TEM} from Pt1AL−Pt-M to Pt2AL−Pt-M was 0.5 nm (M = Fe and Co) and 0.4 nm (M = Ni) with little change in the σ_{d}. This indicates that one atomic layer thickness of Pt skin (ca. 0.5 nm)15 was formed uniformly on every nanoparticle of Pt1AL−Pt-M. Changes in both the total metal loaded and the composition also supported the formation of one additional Pt-skin layer on Pt1AL−Pt-M. Thus, from the analyses of XRD, TG, ICP-MS, and TEM, we have confirmed the formation of Pt2AL−Pt-M/C, as planned.

3.2 ORR activities and H2O2 yields of Pt2AL−Pt-M/C

Figure 3 shows the cyclic voltammograms (CVs) of Nafion-coated Pt2AL−PtFe/C, Pt2AL−PtCo/C, Pt2AL−PtNi/C, and c-Pt/C electrodes in N2-purged 0.1 M HClO4 solution at 65°C. The current was normalized with the mass of Pt loaded on the working electrode. Scan rate = 0.1 V s⁻¹. 3.2 ORR activities and H2O2 yields of Pt2AL−Pt-M/C. Figure 3 shows the cyclic voltammograms (CVs) of Nafion-coated Pt2AL−Pt-M/C and c-Pt/C electrodes in N2-purged 0.1 M HClO4 solution measured at 65°C. All of the CVs of the Pt2AL−Pt-M/C were similar to that of c-Pt/C or polycrystalline Pt. Based on the hydrogen adsorption charge in the CVs, the values of ηCA of Pt2AL−Pt-M/C were calculated to be 100 m^2 g⁻¹ (M = Fe), 77 m^2 g⁻¹ (M = Co), and 82 m^2 g⁻¹ (M = Ni), while that of c-Pt/C was 119 m^2 g⁻¹.

Figure 4 shows hydrodynamic voltammograms for the ORR at these working electrodes in O2-saturated 0.1 M HClO4 solution at 65°C at a mean flow rate U_{in} of 4.6 cm s⁻¹. The small anodic current densities j_{a} (per unit geometric area) observed at the Pt collecting electrodes are ascribed to the oxidation of H2O2. We will discuss the H2O2 yield of the catalysts later. The ORR currents (j_{a}) at the Pt2AL−Pt-M/C working electrodes commenced to increase at more positive potentials.
The rate of electrolyte diffusion limited based on the concentration of dissolved oxygen and the respective of the kind of catalyst, whose value coincides well with the potential of the collecting electrode = 1.2 V. Mean flow rate of electrolyte = 4.6 cm s\(^{-1}\).

Fig. 4. (Color online) Hydrodynamic voltammograms for the ORR in O\(_2\)-saturated 0.1 M HClO\(_4\) solution at Naftion-coated Pt\(_{2}\)AL–PtFe/C, Pt\(_{2}\)AL–PtCo/C, Pt\(_{2}\)AL–PtNi/C, and c-Pt/C electrodes at 65°C and simultaneously acquired current density \(j_1\) at Pt collecting electrodes for the oxidation of H\(_2\)O\(_2\). Potential scan rate = 0.5 mV s\(^{-1}\). Potential of the collecting electrode = 1.2 V. Mean flow rate of electrolyte = 4.6 cm s\(^{-1}\).

Fig. 5. Comparison of kinetically-controlled area-specific activity, \(j_1\) at 0.85 V at the Naftion-coated Pt\(_{2}\)AL–PtFe/C, Pt\(_{2}\)AL–PtCo/C, Pt\(_{2}\)AL–PtNi/C, and c-Pt/C electrodes measured in O\(_2\)-saturated 0.1 M HClO\(_4\) at 65°C, just before (solid bars, initial) and after the accelerated durability test (hatched bars, \(10^4\) cycles). The accelerated durability test was performed in N\(_2\)-saturated 0.1 M HClO\(_4\) at 65°C by applying potential step cycles between 0.6 and 1.0 V (6 s/cycle).

Fig. 6. Comparison of kinetically-controlled mass activity, \(MA_k\) at 0.85 V obtained at the Naftion-coated Pt\(_{2}\)AL–PtFe/C, Pt\(_{2}\)AL–PtCo/C, Pt\(_{2}\)AL–PtNi/C, and c-Pt/C electrodes measured in O\(_2\)-saturated 0.1 M HClO\(_4\) at 65°C, just before (solid bars, initial) and after the accelerated durability test (hatched bars, \(10^4\) cycles).

Fig. 7. Comparison of mass activity \(MA_k\) evaluated on-coated Pt\(_{2}\)AL–PtFe/C, Pt\(_{2}\)AL–PtCo/C, Pt\(_{2}\)AL–PtNi/C, and c-Pt/C electrodes measured in O\(_2\)-saturated 0.1 M HClO\(_4\) at 65°C.
3. Durability of Pt2AL-Pt-M/C to potential changes

We have performed a preliminary durability test by potential-step cycling between 0.6 V and 1.0 V (holding 3 s at each potential, 6 s for one cycle) in N2-purged 0.1 M HClO4 solution at 65°C, which simulates load cycles for FCVs.28 After 104 cycles, CVS and hydrodynamic voltamograms for the ORR were measured to evaluate changes in ECA, jk, MAk, and P(H2O2). The values of jk and MAk at the various catalysts after 104 cycles are shown as hatched bars in Figs. 5 and 6, respectively.

The value of jk at c-Pt/C was nearly unchanged after 104 cycles (Fig. 5), whereas the MAk value decreased severely, to 30% of the initial value (Fig. 6). This is ascribed to the decrease in the ECA due to particle agglomeration.29 It is quite striking that jk at the Pt2AL–PtCo/C remained virtually unaltered, and the retention of MAk was as high as 86%. This indicates that the dealloying was almost completely suppressed by the stabilized Pt-skinc layer of Pt2AL, on the surface, and the agglomeration of the catalyst particles was greatly mitigated. The retention of jk at the Pt2AL–PtFe/C (89%) and Pt2AL–PtNi/C (83%) was moderate, but the retention of MAk (57 to 55%) was ranked between those of Pt2AL–PtCo/C and c-Pt/C. However, the very high initial jk value for the Pt2AL–PtNi/C is still highly attractive, particularly, if we can mitigate the particle agglomeration and further suppress the dealloying. It is very important to analyze the differences in the degradation mechanisms among these catalysts, which can provide a clue for designing highly active, highly durable catalysts. Such studies are in progress in our laboratory.

4. Conclusions

We have succeeded in preparing potential cathode catalysts for PEsFCs, i.e., carbon-supported Pt-M (M = Fe, Co, and Ni) alloy nanoparticles with two atomic layers of Pt-skinc (Pt2AL). Multiple analyses by XRD, ICP-MS, TG, and TEM convinced us of the formation of monodisperse Pt2AL-Pt-M/C. The Pt2AL–PtNi/C catalyst exhibited the highest initial performance: jk = 2.13 mA cm⁻² (4.3 times higher than that of c-Pt/C) and MAk = 1960 A h g⁻¹ (3.3 times higher than that of c-Pt/C) at 0.85 V and 65°C in O₂-saturated 0.1 M HClO4. In a preliminary durability test of 10⁴ potential cycles between 0.6 V and 1.0 V, the Pt2AL–PtCo/C showed exceptional properties, maintaining the jk value unchanged and mitigating the particle agglomeration. The inferior durability observed at the Pt2AL–PtFe/C and Pt2AL–PtNi/C electrodes might be ascribed to an imperfect formation of Pt2AL, since dealloying was not completely suppressed, leading to a decrease in jk. Hence, an optimization of the preparation protocol for Pt2AL–PtFe/C and Pt2AL–PtNi/C, together with an analysis of the degradation mechanism, can provide us clues for designing catalysts with higher activity and higher durability.

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References

21. The value expected for a single atomic layer of bulk Pt would be between 2 x 0.196 = 0.392 [100] direction) to 2 x 0.226 = 0.452 nm [111] direction), but surface layers can exhibit slight expansion, particularly for nanoparticles.

Table 2. H₂O₂ yield, P(H₂O₂), at 0.70 V and 0.80 V just before (initial) and after the durability test (10⁴ cycles).

<table>
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<tr>
<th></th>
<th>Initial</th>
<th>10⁴ cycles</th>
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<tr>
<td></td>
<td>0.70 V</td>
<td>0.80 V</td>
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<tr>
<td>Pt₂AL-PtFe/C</td>
<td>1.0</td>
<td>0.2</td>
</tr>
<tr>
<td>Pt₂AL-PtCo/C</td>
<td>0.5</td>
<td>0.3</td>
</tr>
<tr>
<td>Pt₂AL-PtNi/C</td>
<td>0.4</td>
<td>0.2</td>
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<tr>
<td>c-Pt/C</td>
<td>0.5</td>
<td>0.2</td>
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