Pt-flecks on colloidal Au (Pt\(^{\text{Au}}\)) as nanostructured anode catalysts for electro-oxidation of formic acid

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The study of electrocatalytic oxidation of C1 molecules such as methanol and formic acid on Pt-based electrocatalysts is of ongoing interest, not only for using them as the practical fuels for polymer electrolyte membrane fuel cell (PEMFC) technologies, but also for providing mechanistic insight into the electro-oxidation of small organic molecules. Unlike the electro-oxidation of methanol which would inevitably occur through an indirect pathway of poisonous intermediates oxidation, the electro-oxidation of formic acid could also proceed from a direct pathway via reactive intermediates. The availability of HCOOH electro-oxidation via direct pathway could be significantly influenced by the dispersion state of Pt. It is therefore valuable to investigate the electro-oxidation of HCOOH by systematically changing the dispersion state of Pt in electrocatalysts. In our previous work, we obtained two series of nanostructured Pt-on-Au particles (coded as Pt\(_m^{\text{Au}}\), \(m\) being the atomic Pt/Au ratio) by depositing Pt on Au colloidal particles with two average sizes (i.e., Au-I: 10.0 ± 1.2 nm, Au-II: 3.0 ± 0.6 nm). Characterizations of Pt\(_m^{\text{Au}}\) particles with UV-Vis, TEM, XPS, XRD and SERS demonstrated that the dispersion state of Pt deposits could be gradually changed from a shell-like overlayer to two-dimensional rafts or very small flecks (≤ 1 nm) of Pt clusters on Au particles by the control of \(m\) in Pt\(_m^{\text{Au}}\) particles, as shown in Figure 1. Reported here are our investigation to employ such Pt\(_m^{\text{Au}}\) particles with gradual change in the dispersion state of Pt as anode catalysts for formic acid electro-oxidation.

![Figure 1](image-url)

Cyclic voltammetric (CV) scanning measurements were performed in 0.5 M H\(_2\)SO\(_4\) electrolyte containing 2.0 M HCOOH to compare HCOOH electro-oxidation behavior over samples (Figure 2). The electro-oxidation behavior of formic acid was found very sensitive to the morphology and dispersion (utilization) of Pt deposits on the Au nanoparticles: Pt\(_m^{\text{Au}}\)/C catalysts containing isolated Pt-flecks (i.e., Pt\(_m^{\text{Au-I}}\) at \(m < 0.2\) and Pt\(_m^{\text{Au-II}}\) samples) with high Pt utilization (> 40%) showed a distinct main peak at ca. 0.40 V (vs. SCE, Peak-I); but Pt\(_m^{\text{Au}}\)/C samples containing Au colloids that were fully covered with Pt (i.e., Pt\(_m^{\text{Au-I}}\) at \(m > 0.2\)) at low Pt utilization (< 20%) showed a small peak ca. 0.75 V (vs. SCE, Peak-II), which was
similar to performance of the traditional Pt/C catalyst. The mass-specific activity and the areal activity of Pt at 0.40 V in the Pt\textsuperscript{m}\textsuperscript{Au} catalysts containing only Pt-flecks on Au colloids (Pt utilization > 50\%) \footnote{1} were, respectively, at least 25 times and 5 times higher than those of conventional Pt/C and “core@shell” (Au@Pt) structured Pt\textsuperscript{m}\textsuperscript{Au} catalysts (i.e., Pt\textsuperscript{m}\textsuperscript{Au-I at }m > 0.2), indicating that the catalytic activity of Pt\textsuperscript{m}\textsuperscript{Au/C catalysts for formic acid electro-oxidation could be dramatically enhanced by decreasing the domain size of Pt deposits or increasing the Pt dispersion on Au particles. When compared at similar Pt dispersions, the intrinsic activity (or areal activity) of Pt-flecks on Au-II (3.0 ± 0.6 nm) particles (Pt\textsuperscript{m}\textsuperscript{Au-II}) was found almost 4 times higher than that of Pt-flecks on Au-I (10.0 ± 1.2 nm) particles (Pt\textsuperscript{m}\textsuperscript{Au-I}), revealing that smaller Au particles can serve as effective “activity-promoter” to the Pt-flecks on their surfaces.

The electro-oxidation of formic acid on Pt\textsuperscript{m}\textsuperscript{Au/C catalysts was further investigated by increasing HCOOH concentration from 0.2 to 3.2 M with a stepwise increment of 0.2 M in 0.5 M H\textsubscript{2}SO\textsubscript{4} solutions. The highest level of current was observed in a certain HCOOH concentration range on Pt/C and both Pt\textsuperscript{m}\textsuperscript{Au/C catalysts (Figure 3). Therefore, the determination of an appropriate concentration window for formic acid fuel can be a key to maximizing the power densities of direct formic acid fuel cells using Pt-based electrocatalysts.

In conclusion, Pt-flecks on gold colloids can be exploited as advanced nanostructures for activity enhancement of Pt in electrocatalysts for the electrooxidation of formic acid. The electrocatalytic activity of Pt\textsuperscript{m}\textsuperscript{Au/C depends not only on Pt dispersion (utilization) but also on sizes of the underlying Au colloids.

References