

Individual nanoparticles of fuel cell electrocatalysts: preparation and probing the oxygen reduction reaction

Shengli Chen and Anthony Kucernak*

Department of Chemistry, Imperial College of Science, Technology and Medicine, London SW7 2AZ, UK

Pt and Pt-based alloy particles of nanometer size supported on carbon are the most widely used active catalysts in state-of-the-art polymer electrolyte fuel cells. There has been a great interest in the relation between the activity of such catalyst electrodes towards fuel cell relevant reactions and the size of the supported catalyst particles. A better understanding on the size effects of catalyst particles on their electrocatalytic properties relies on strictly monodispersed particle size. However, supported catalyst particle assemblies always show relatively broad size distributions. The results obtained on such particle assembly electrodes therefore are not entirely reproducible¹⁻². An alternative and novel approach to probe the size-related properties is to use individual particles. Preparation and manipulation of individual nanoparticles is of great significance in nanoscience, especially for understanding the size tunable properties of nanoparticles. Accurate size control and the measurements of the reactivity of individual nanoparticles, is still a challenging task in which complicated techniques are required e.g., STM tip transfer technique³⁻⁴. In this paper, we report a straightforward way to prepare single Pt and Pt based alloy nanoparticles supported on carbon substrates and the results of the oxygen reduction reaction studied using these small single particle electrodes.

We use the insulated carbon electrodes having exposed electroactive areas on the nanometer scale as a supporting substrate⁵⁻⁶. The Pt or Pt based alloy is introduced onto the surface of these substrates by electrodeposition. Since the active area of the substrate is extremely small, it is possible that only one nucleus forms and grows during the deposition process, thus forming a single catalyst particle supported on carbon. The particle size can be controlled by stopping the deposition at specific current or charge. Figure 1 gives SEM images of several typical Pt particles prepared using the present method. These carbon supported Pt particle electrodes are very similar to the active catalyst electrodes in fuel cell but have a much smaller structural complexity. The electrodes have features like high Pt loading, single particle size and defined mass transport conditions.

The oxygen reduction reaction has been investigated using these single catalyst particle electrodes. We have explored the particle size effects on the reaction pathways and kinetics. In this paper we show that the catalyst particle size may affect the oxygen reduction reaction (ORR) pathway via modulating the mass transport rate.

However, such an effect of particle size on reaction mechanism only occurs when the particle radius is between 50nm and 5 μ m. When the particle is larger than 5 micrometers, the formation of hydrogen peroxide is negligible and the ORR is seen to proceed through entirely a 4 electron reaction. At particles smaller than 50nm, the formation rate of hydrogen peroxide becomes almost independent on the particle size due to the high mass transport rate with the formation rate of hydrogen peroxide governed by the adsorption/desorption equilibrium of peroxide intermediates. This implies that the electrocatalytic activity of fuel cell catalyst electrodes toward oxygen reduction reaction should increase with decreased size of catalyst particle in the view of the optimum diffusion of reactants around individual particles, as argued by Watanaba et al.¹ It is also shown that the kinetics of the ORR is rather more complex than usually believed. Anion adsorption may affect the ORR not only by blocking surface sites, but also through changing the potential profile inside the double layer. The ORR on electrocatalytic electrodes strongly depends on the potential profile in the double layer since inner-sphere electron-transfer steps are involved. The size of catalyst particle may affect the oxygen reduction kinetics via double layer effects since the potential distribution inside the double layer around a catalyst particle is tunable by the particle size. So, when considering particle size effects on reaction kinetics, one must also consider the double layer.

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Figure 1. The SEM images of Pt single particles electrodeposited on small carbon substrates. The diameters of the Pt particles are about 500nm (a), 300nm (b) and 150nm (c) respectively.

