

ELECTROCHEMICAL CHARACTERIZATION OF HIGH AREA PLATINUM DISPERSED ON THE SURFACE OF A GLASSY CARBON ROTATING DISK ELECTRODE IN THE ABSENCE OF BINDERS OR OTHER ADDITIVES

Yibo Mo, S.Sarangapani, Anh Le, and Daniel A. Scherson

Department of Chemistry
Case Western Reserve University
Cleveland, OH 44106-7078

ICET, Inc.
916 Pleasant Street
Unit # 12
Norwood, MA 02062

INTRODUCTION

Electrode materials in high area form are of common use in electrochemical energy storage and energy generation applications as in batteries and fuel cells. Attempts to extract information regarding intrinsic properties of such highly divided materials in environments that resemble actual devices are often compromised by the presence of binders and/or additives, including complications derived from mass transport hindrances and potential distribution associated with often highly convoluted structures. Efforts toward eliminating some of these problems have been implemented in our laboratory using the embedded particle technique for both electrochemical and spectroelectrochemical measurements,¹ and also by the elegant approach introduced by Uchida et al.² who relied on micromanipulators to isolate the electrochemical response of single particles a few tens μm in diameter.

Ingenuous methods have also been described to examine far smaller Pt particles of the type used in fuel cells dispersed on smooth carbonaceous supports. For example, Schmidt et al.³ immobilized high area Pt dispersed on the surface of a glassy carbon rotating disk electrode (RDE) by placing a layer of Nafion on the surface allowing measurements of solution phase hydrogen oxidation to be performed at rotation rates of up to 3600 rpm.³ More recently, Weaver and Wieckowski used Pt dispersions on GC without a Nafion overlayer to monitor in situ, infrared spectra of adsorbed CO as a function of the applied potential⁴. The results to be presented in this work indicate that carefully dispersed high area Pt on the surface of a GC RDE of a GC/Pt ring disk electrode assembly displays good adherence without the need of a Nafion overlayer even when rotated for minutes at rates of up to 2500 rpm as judged by quantitative coulometry of cyclic voltammetric curves recorded before and after rotation. Furthermore, dynamic polarization curves for O₂ reduction in aqueous 0.5 M H₂SO₄ yielded results bearing close resemblance to on Pt dispersed on GC-RDE surface covered with a Nafion layer under otherwise identical conditions and also to those observed on a solid Pt electrode in 0.5 M H₂SO₄.

EXPERIMENTAL

Experiments were performed either with GC/Pt or Pt/Pt RRDE electrodes (Disk area: 0.1642 cm² Pine Instruments) in 0.5 M H₂SO₄ prepared from Ultrex acid and ultrapurified water (Barnstead). High area Pt (Alfa Aesar, Item #12755, S.A. nominally 27 m²/g) was dispersed on the surface of the GC disk electrode by first agitating ultrasonically 10 mg Pt black in 1.0 mL of water. About 10~15 μL of the resulting suspension were then placed on the GC surface following by drying using a very gentle stream of Ar (UHP, PRAXAIR). After rinsing with pure water, the Pt loading procedure was repeated twice to achieve a more uniform Pt layer. The actual area of the Pt particles adhering to the GC surface was determined from cyclic voltammetry by well-known

coulometric procedures, using the hydrogen adsorption/desorption features as a basis. For some of the experiments, the dispersed Pt layer was covered with a layer of Nafion following the method described by Schmidt et al.³ Oxygen reduction measurements were performed in O₂ (PRAXAIR, 99.6%)-saturated 0.5 M H₂SO₄ solutions in the dynamic polarization mode at a scan rate of 20 mV/s at rotation rates in the range 100 to 2500 rpm. Similar measurements were also performed using a Pt/Pt RRDE to compare the results with those obtained for the dispersed Pt/GC specimens. Hydrogen peroxide generated at the various electrodes was collected by polarizing the smooth Pt ring a +1.40 V a potential at which H₂O₂ undergoes oxidation under diffusion limited conditions.

RESULTS AND DISCUSSION

Cyclic voltammetry (upper curve) and dynamic polarization curves for O₂ reduction (middle curves) and H₂O₂ collection (lower curves) for high area Pt dispersed on GC (1.3 mC/cm²) recorded in Ar-purged and O₂-saturated 0.5 M H₂SO₄, respectively, are shown in the left Panel Fig. 1. Corresponding curves obtained for a similar Pt dispersion on GC (6.4 mC/cm²) covered with a layer of Nafion are given in the middle panel in this figure. Also shown for comparison are data collected under otherwise identical conditions with a solid Pt/Pt RRDE in O₂-saturated 0.5 M H₂SO₄ (see Right Panel). The fact that the limiting currents both for the bare and Nafion covered Pt dispersed on GC are somewhat smaller than those observed for the massive specimen reflect in all likelihood, smaller effective areas due to the low overall dispersion compared to a solid metal disk. The loss of active material in bare dispersed high area Pt on GC, as evidenced by cyclic voltammetric curves obtained by purging the 0.5 M H₂SO₄ solution with Ar following oxygen reduction measurements, was found to be negligible. Overall, the technique described in this work may find wide applications in studies aimed at characterizing a wide variety of electrocatalysts in high area form. In addition, the feasibility of modifying dispersed Pt on GC in situ has been demonstrated using the adsorption of Se as a model system.

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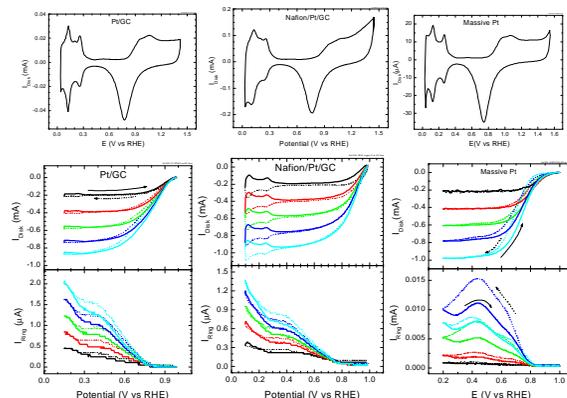


Fig.1 Cyclic voltammograms of Pt electrodes and polarization curves of oxygen reduction and hydrogen peroxide detection. Scan rates: 20mV/s, rotation rate: 100, 400, 900, 1600, 2500 rpm.