Sequential and Simultaneous Electrodeposition of Pt-Ru Electrocatalysts on HOPG, GC, and GDL Substrates

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In the electrodeposition of Pt-Ru electrocatalyst particles on various substrates, it is common to deposit both metals simultaneously. However, the present work will show that there are advantages of depositing these metals sequentially, Pt first and Ru second. The influences of Ru concentration on the electrodeposition by both the sequential and simultaneous linear sweep potential techniques with Pt were studied on previously activated HOPG substrates. Sequential voltammetric results allowed us to determine not only the loadings of Pt and Ru, but also to carry out a complete quantitative catalytic evaluation, which is ordinarily difficult, i.e, when simultaneous deposition is used. Morphological and microscopic characterization, carried out with scanning electron microscopy (SEM), and atomic force microscopy (AFM), showed that, in general, the deposits are clusters of aggregated particles. Scanning tunneling microscopy (STM) showed that the tops of these clusters are from 5 to 10 nm in diameter. The distributions of these clusters on the HOPG surface were heterogeneous and disperse. For both types of deposition, the Ru present on the surface produced changes in the dimensions (diameter and height) of the clusters as compared to pure Pt clusters. XPS data suggested that the Pt-Ru surfaces are generally enriched in Pt. For the Ru component, metallic Ru and either RuOx or $Ru(OH)_x$ were the chemical species present. The surface concentration of the Ru component decreased remarkably after methanol oxidation experiments, due to dissolution at the relatively high potentials employed. Electrocatalytic examination of methanol oxidation, carried out by cyclic voltammetry and chronoamperometry, showed that the oxidation current densities for the Pt-Ru electrodes were enhanced by factors of at least two compared to the pure Pt clusters. Finally, the results indicated that the electrodeposition technique with linear sweep potential allowed us to obtain highly electrocatalytic surfaces, based on optimal Ru surface concentration as well as high dispersion.

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Pt-Ru* (seq.)	Mean diameter (nm)	Mean height (nm)	Density (particle /μm^2)	Roughness AFM/ (nm)
Pure Pt	**411**	**103**	**1.2**	**72**
1:1	366	86	1.9	46
1:0.5	345	84	1.6	47
1:0.1	278	55	2.6	59
1:0.05	284	45	1.4	93
Pt-Ru* (sim.)				
1:1	284	59	2.4	58
1:0.5	406	58	0.81	37
1:0.1	284	29	1.1	34
1:0.05	395	116	1.1	35

Table 1: Morphological data from AFM images taken at a 10 x 10 μm^2 area from sequential and simultaneous electrodeposition of Pt-Ru on HOPG. (*Pt/Ru concentration ratios from the solutions used for the electrodeposition.)

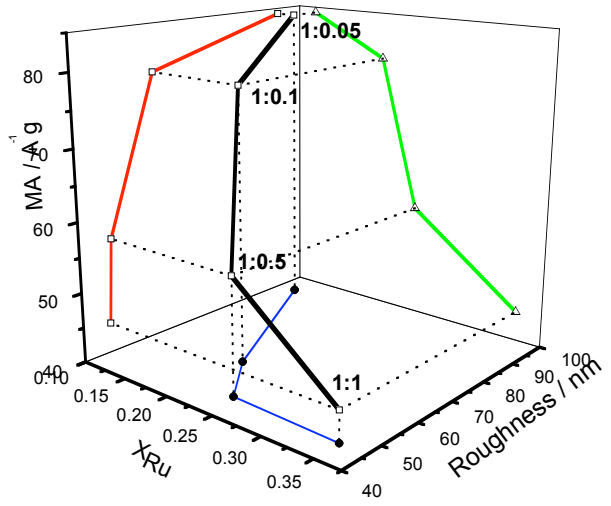

Figure 1. Three-dimensional plot of mass activity (MA) for methanol oxidation, evaluated from cyclic voltammetric data for sequentially deposited Pt-Ru electrodes, as a function of AFM roughness (evaluated from 10 μm × 10 μm areas) and Ru surface mole fraction (evaluated from XPS data). The Pt:Ru solution concentration ratios are indicated in the figure.

ACKNOWLEDGEMENTS

The authors acknowledge the financial support of the ARL Collaborative Technology Alliance in Power and Energy, Cooperative Agreement No. DAAD19-01-2-0010.

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