

RADIOACTIVE LABELING STUDY OF ADSORPTION OF CO POISON ON NOVEL DMFC ANODE CATALYSTS

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Combined radioactive labeling and electrochemical measurements were conducted to study adsorption and desorption of methanol-derived surface CO on fuel-cell grade catalysts. The catalysts used were ruthenium-decorated platinum nanoparticles of various Ru content, obtained by spontaneous deposition. The data from these Pt/Ru surfaces were compared to that obtained with clean platinum nanoparticles. The adsorption results were obtained under constant potential, and the experiments were carried out in sulfuric acid solutions containing methanol (at room temperature). The rates of desorption were also measured at constant potential, after removing the adsorption precursor (methanol) from the solution. The onset potentials of CO desorption were determined under slow potential scan conditions. Adsorption, and desorption were significantly different on Pt/Ru than on Pt, even for the lowest Ru content catalysts. They were also greatly dependent on the Ru packing density on the catalyst surface.

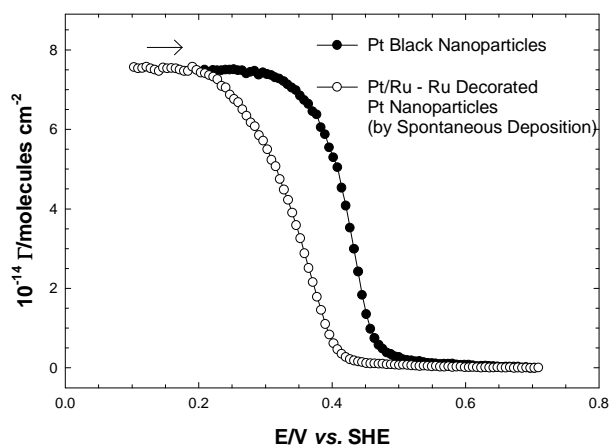


Figure 1. The effect of Ru addition on the onset potential of CO desorption. CO adsorption from 10^{-2} M methanol solution in 0.1 M H_2SO_4 at 0.1 V was followed by solution replacement with supporting electrolyte, and then a slow positive going potential scan (0.1 mV s^{-1}) was initiated.

Radioactive labeling data of surface CO oxidation on platinum black and ruthenium decorated platinum nanoparticles obtained under slow-scan polarization conditions is shown on Figure 1. CO was adsorbed on the catalyst surface from 10^{-2} M methanol (^{14}C labeled) in 0.1 M H_2SO_4 at 0.1 V vs. SHE. Once a constant CO coverage, corresponding to surface concentration of $7.5 \cdot 10^{14}$ molecules cm^{-2} was attained, methanol solution was replaced with the clean (methanol and CO free) supporting electrolyte, the surface concentration was re-checked, and the positive-going potential scan of 0.1 mV s^{-1} was applied. The data show that within the most part of the hydrogen region there is no CO desorption from the surface, and neither is significant change in coverage between pure Pt and Pt/Ru. The latter is in contrast to data obtained with the Pt/Ru alloy nanoparticle electrode where the maximum CO

coverage on platinum/ruthenium was half of that on pure Pt [1]. The CO desorption does not begin until 0.3 V on platinum black, as no drop in the count rate is seen below this potential (Figure 1). However, on platinum/ruthenium the CO desorption is initiated at 0.1 V more negative potential showing that there is about a 0.1 V reduction in the energy to remove CO from the Pt/Ru surface. The Γ vs. E branch is even more negatively shifted with the higher deposited Ru coverage up to the maximum value of 0.2 V, similar to the data obtained with the Pt/Ru alloy nanoparticle in the previous study [1]. Similar separations were observed on the Pt(111) electrode decorated by ruthenium regardless whether the CO adlayer was created from methanol or from a gaseous CO precursor (and desorption was carried out to the clean supporting electrolyte) [2].

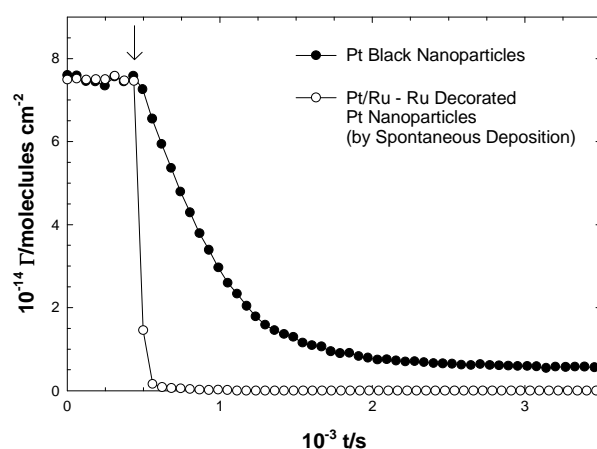


Figure 2. The kinetics of desorption of CO into methanol free solution. Adsorption of CO from 10^{-2} M methanol solution in 0.1 M H_2SO_4 at 0.1 V was followed by solution replacement with supporting electrolyte, and a potential step to 0.42 V, at the point indicated with the arrow.

Further support for the strong effect of surface ruthenium on the CO oxidation process is provided by the data in Figure 2. The beginning of the experiment was the same as reported above, and the constant surface concentration of CO was measured at 0.1 V vs. SHE in the clean supporting electrolyte. Next, instead of applying the slow-scan polarization, the potential was stepped to 0.42 V, that is the one in the range that is common to the two surfaces under dynamic desorption conditions. It is shown in Figure 2 that the oxidative CO desorption is much faster on Pt/Ru than on Pt, and that the desorption from the latter catalyst is incomplete. Clearly, the significant difference in the stability of the CO on these two surfaces measured at a constant electrode potential is observed.

Acknowledgements

This work was supported by the Los Alamos National Laboratory DOE LANL 30167010139. We also acknowledge support from an exchange program between CNRS (France) and the University of Illinois, including contribution by F. Hahn to this project.

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