

Surface Chemistry and Oxygen Reduction Reaction on Pt and Pt - Bimetallic Surfaces

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In this report we present recent progress in the development of the fuel cell cathode materials. The focus of the work is related to surface characterization, surface chemistry, kinetics, reaction mechanism and peroxide formation. Platinum single crystals have been used in order to provide insight into the effects of the surface structure on the kinetics of the Oxygen Reduction Reaction (ORR), and to establish a fundamental link and ratio between the Specific Activity (mA/cm^2) of single crystalline surfaces and polycrystalline materials.

Polycrystalline PtM alloy ($M = \text{Ni, Co, Fe, V, Cr, Ti, Ru}$) electrodes were prepared in ultra-high vacuum by sputtering/annealing cycles, respectively. Before the transfer to an electrochemical environment (0.1M HClO_4), the PtM alloys were characterized in UHV by Auger electron spectroscopy (AES), Low Energy Ion Scattering (LEIS) and soft x-ray photoelectron spectroscopy (XPS) by using synchrotron radiation source. After exposure to the electrolyte during potential controlled experiments the alloy surfaces were transferred back to UHV in order to detect the surface composition.

The UHV characterization of the alloys shows in most cases different surface composition after annealing in comparison to the bulk composition (sputtered surface) due to segregation. We have found complete enrichment of Pt as outermost layer for Pt_3Co and Pt_3Ni samples, the so called Pt-skin composition. Establishing the electronic properties of Pt-skin and surfaces with bulk compositions by XPS it was revealed that d-band center has been shifted versus Fermi level which could have significant impact on adsorptive and catalytic properties.

The electrochemical characterization shows that most of the bimetallic alloy surfaces have higher Specific Activity for ORR than a pure polycrystalline Pt. The highest value established for ORR at 0.85 V vs. reversible hydrogen electrode (RHE) was measured for a Pt-skin surface on the Pt_3Co alloy.

The results on Pt single crystals show that the structure sensitive kinetics of the ORR follow the order: $\text{Pt}(100) < \text{Pt}(111) < \text{Pt}(110)$. Values of specific activities of polycrystalline Pt at 0.85 V correspond to the mean value of single crystal activity.

Peroxide formation, reaction mechanism and activation energy of all samples are Pt like and essentially the same. Kinetics are mainly determined by the $(1-\Theta)$ term in kinetic equation i.e. the surface coverage of adsorbed spectator species like oxides, anions etc. vary for different samples which affects the number of active Pt sites for O_2 adsorption. Therefore the significant improvement of the ORR kinetics on Pt based alloy systems is due to the inhibition of Pt-OH formation beyond 0.8 V , which is a consequence of modified electronic structure of the d-band center.

Characterization of bimetallic surfaces in UHV by AES and LEIS after electrochemical treatment show

complete dissolution of the non-Pt component. This finding has important impact to the surface chemistry of Pt based alloys and brings a new lighting to the fuel cell cathode materials. The Surface formed after dissolution of non noble components is so called Pt-skeleton and this is the surface where ORR takes place.