Hot electron flux at the solid-liquid interfaces; effects of pH and concentration during decomposition of hydrogen peroxide

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An in-depth understanding of chemical reactions occurring at solid-liquid interfaces is crucial for a large number of technological processes. These include heterogeneous catalysis. electrochemistry, corrosion, environmental science, development of energy sources, and others. At the same time, our knowledge about the processes which take place on the solid surfaces in a liquid medium remains incomplete. The main reason for this is that most of the conventional surface science methods are based on the use of various particles (electrons, ions, or atoms) to probe the surface. These methods work well under ultrahigh vacuum conditions. However, the use of them for the study of solid-liquid interfaces is limited due to the issues associated with the mean free path of the particles. Therefore, new experimental methods free from the above problems are needed [1].

In this talk, we report on the use of internal emission of hot electrons for the study of solid-liquid interfaces under decomposition of hydrogen peroxide (H_2O_2) . The principle behind the method is depicted in Fig. 1. Hot electrons are generated on the surface of a metal-semiconductor catalytic nanodiode when an exothermic chemical reaction takes place [2]. The metal film thickness is smaller than the electron mean free path. Therefore, hot electrons can reach the Schottky contact at the MS boundary without attenuation. surmount the barrier and generate an electric current, called chemicurrent. The chemicurrent can be used to monitor the surface chemistry in real time [2]. We show experimental results

obtained using this method for the case of decomposition of H_2O_2 on platinum catalysts. Fig.2 shows a typical chemicurrent transient measured during decomposition of aqueous H_2O_2 on the Pt/n-Si nanodiode. By conducting experiments in H_2O_2 solutions with different acidity (see inset in Fig.2) we show a clear link between the chemicurrent magnitude and the rate of formation of hydroxyl radicals on the Pt surface. The presence of hydroxyl radicals was confirmed with the Fourier transform infrared spectroscopy measurements.



Fig.1 Probing solid-liquid interfaces with hot electrons during the decomposition of aqueous H_2O_2 on Schottky nanodiodes. Here, (1) is the generation and (2) transfer of a hot electron across the metal-semiconductor contact.



Fig. 2 Typical chemicurrent transients during decomposition of aqueous H_2O_2 on the Pt/n-Si nanodiode. Inset: Dependence of the chemicurrent magnitude on the acidity of the H_2O_2 solution.

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