



Hot electron flux at solid–liquid interfaces probed with Pt/Si catalytic nanodiodes: Effects of pH during decomposition of hydrogen peroxide

Seung Hee Lee^{a,b,1}, Ievgen I. Nedrygailov^{a,1}, Sunyoung Oh^{a,b}, Jeong Young Park^{a,b,*}

^a Center for Nanomaterials and Chemical Reactions, Institute for Basic Science, Daejeon 305-701, Republic of Korea

^b Graduate School of EEWS, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Republic of Korea

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ABSTRACT

Hydrogen peroxide (H_2O_2) is an effective oxidizing agent that is commonly used in industry. In the presence of metal catalysts, H_2O_2 can decompose into water and oxygen. Understanding this process at a fundamental level is extremely important for a number of industrial applications, e.g. the direct synthesis of H_2O_2 from H_2 and O_2 . Here, we studied the rates of H_2O_2 decomposition on Pt/n-Si catalysts using a chemi-current approach that is based on the detection of hot electrons created during dissociative adsorption of H_2O_2 molecules on platinum. We showed that both the rate of H_2O_2 decomposition and the corresponding chemi-current are sensitive to the pH of the reactive solution. This phenomenon is explained by variation of the potential barrier for electron transfer at the Pt/solution interface caused by adsorption of H^+ and OH^- species from the solution on the catalytic surface.

1. Introduction

Hydrogen peroxide (H_2O_2) is an effective and environmentally friendly oxidizing agent that is commonly used in industry for pulp and paper bleaching, wastewater treatment, textile production, chemical synthesis, and many other applications [1–7]. Since the primary by-products of reactions involving H_2O_2 are water and oxygen, it is often called the most environmentally friendly oxidant available. Currently, H_2O_2 is produced by the indirect oxidation of H_2 (the so-called anthraquinone auto-oxidation (AO) process), which consumes large amounts of energy and requires the use of toxic solvents [1–5,7,8]. In addition, application of the AO process is only economically feasible for large-scale production. This implies that it is not applicable for one-pot synthesis when H_2O_2 is produced and consumed in the same reactor to obtain an enhanced overall efficiency of the chemical reaction. Thus, the development of a new, cost-effective, and clean process producing H_2O_2 is critical.

There are several alternatives to the AO process discussed in the literature, including the oxidation of alcohols, electrochemical synthesis, the plasma method, and direct synthesis from H_2 and O_2 [1,4,7]. Among these, the direct synthesis of H_2O_2 from H_2 and O_2 is considered the most simple and promising process to produce H_2O_2 in small quantities right where it will be used [2,4–6,9–12]. As shown in Fig. 1a (Reaction 1), this process is thermodynamically favorable and highly

exothermic. It is conducted in a liquid medium in the presence of supported metal catalysts (mainly Pd, Pt, and Au) [1,8,12,13]. However, despite the obvious advantages over the AO process, there are a number of problems that make commercialization of the direct synthesis of H_2O_2 difficult at the present time [4,8,10–12,14]. One of them is related to the low selectivity for H_2O_2 formation caused by the parallel process of water formation (Reactions 2–4 in Fig. 1a). One of these reactions, i.e. the decomposition of H_2O_2 (Reaction 2 in Fig. 1a), is even more thermodynamically favorable than the direct synthesis of H_2O_2 from H_2 and O_2 , and takes place on the same catalyst used to produce H_2O_2 . A significant amount of research has focused on solving this problem. It was found that the selectivity of the direct synthesis of H_2O_2 can be adjusted by changing the pH of the reaction medium [8,11,14–16]. In particular, there are multiple reports that the selectivity of H_2O_2 synthesis increases when the process is carried out in solutions with high acidity. It is believed that this effect can be explained by the transfer of electric charge between the adsorbed protons and the catalytic surface, which affects interactions between the H_2O_2 molecules and the catalyst [2,8,14,15,17]. However, this hypothesis requires experimental verification, which is a difficult task because the aqueous medium screens the interactions between the catalytic surface and the adsorbate. Conventional methods of surface science cannot help to solve this problem because they were designed to work in a high vacuum [18]. Despite recent advances in the adaptation of some of

* Corresponding author at: Graduate School of EEWS, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Republic of Korea.

E-mail address: jeongypark@kaist.ac.kr (J.Y. Park).

¹ Authors contributed equally to this work.

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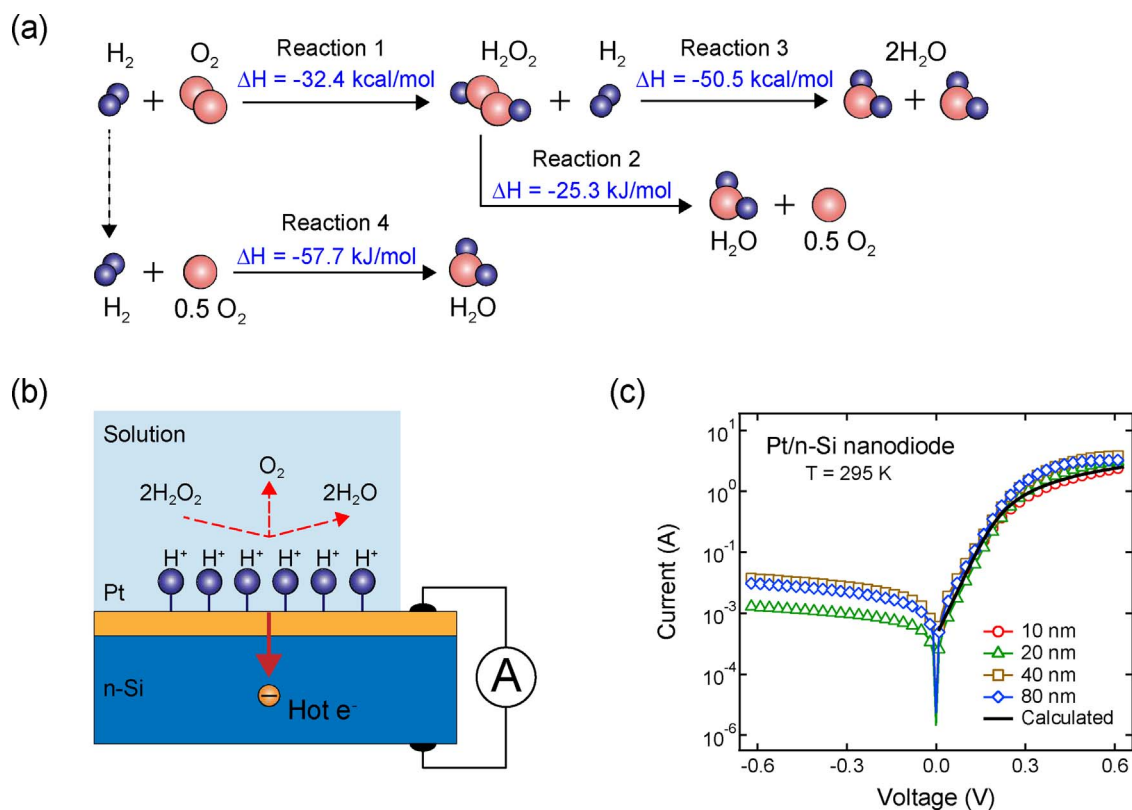


Fig. 1. (a) Reactions involved in the direct production of H_2O_2 from H_2 and O_2 . Adapted from Ref. [1]. (b) Principle of detecting hot electrons during the decomposition of aqueous H_2O_2 on a Pt/n-Si catalytic nanodiode. (c) Typical current–voltage curves measured from Pt/n-Si catalytic nanodiodes with varied Pt film thickness.

these methods, e.g. X-ray photoelectron spectroscopy, to probe the interface between the liquid and solid phases, only vapor–solid or liquid–solid interface where the thickness of the liquid film is on the order of tens of nanometers can be studied at the present time [18,19]. These conditions, however, are far from what is observed in real chemical reactors. An alternative method for studying processes occurring at liquid–solid interfaces under reaction conditions was proposed in ref. [20,21]. This method is based on the detection of energetic (hot) electrons created in a metal catalyst during exothermic chemical reactions as a result of non-adiabatic energy transfer using thin film metal–semiconductor Schottky diodes, known as catalytic nanodiodes. Since the processes of hot electron generation and transport occur inside the catalytic nanodiode, this method can be applied to study chemistry at liquid–solid interfaces at conditions close to those found in real chemical reactors.

Here, we attempt to shed light on the role of charge transfer on the rate of H_2O_2 decomposition in solutions with different pH values using Pt/n-Si nanodiodes. The main idea of the method is outlined in Fig. 1b. The decomposition of H_2O_2 when catalyzed on the Pt surface leads to the creation of hot electrons [20,21]. These electrons are highly energetic and can travel distances on the order of tens of nanometers without significant energy losses [22–27]. Consequently, they can be captured using thin-film ($d = 10$ nm) Pt/n-Si catalytic nanodiodes. The signal detected by the catalytic nanodiodes is called a chemicurrent and it provides valuable information on the rate of charge transfer during the adsorbate–surface interactions. Thus, in combination with the data on the acidity of the reaction medium and the rate of chemical reaction, detection of chemicurrent can aid in understanding the effect of charge transfer on the selectivity of direct H_2O_2 synthesis in solutions with different pHs.

2. Experimental procedures

2.1. Liquid–phase catalytic reactor

The apparatus for the chemicurrent measurements during the catalytic decomposition of H_2O_2 on the surface of Pt/n-Si nanodiodes is described in detail elsewhere [21]. In brief, the sample cell with the H_2O_2 solution was equipped with a linear motion feedthrough that allows for immersion of the catalytic nanodiode into the solution to initiate the decomposition reaction and to remove the nanodiode from the solution at the end of the experiment. The chemicurrent was measured using a Model 2400 Series SourceMeter from Keithley Instruments, Inc. To determine the reaction rate, the amount of O_2 released in the H_2O_2 decomposition was measured as a function of time using a 120AA Baratron high-accuracy absolute-capacitance manometer from MKS Instruments. The composition of the gaseous atmosphere in the catalytic reactor during the experiments was controlled by a quadrupole mass spectrometer gas analysis system HPR-20 QIC from Hidden Analytical Limited.

2.2. Catalytic nanodiodes

Planar Pt/n-Si nanodiodes were fabricated by e-beam deposition of metal contacts onto the polished surface of n-type Si (100) substrates ($\rho = 1\text{--}10 \Omega\text{-cm}$). First, the Si substrates were etched in a buffered oxide solution composed of NH_4F and HF in water for 150 s at room temperature. Next, the ohmic contacts were fabricated on the Si surface by deposition of 50 nm thick Ti films, followed by 50 nm thick Au films through a $5 \times 5 \text{ mm}^2$ stainless steel mask. At the final stage, Pt thin films with a contact area of 0.8 cm^2 and thicknesses of $d = 10\text{--}80$ nm were deposited. The quality of the Pt films after deposition was controlled using atomic force microscopy, see Fig. 2.

To obtain the properties of the Schottky barrier at the Pt/n-Si

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