

## Electrochemical Reactivity of Chemically Roughened Tungsten Electrodes†

IN-TAE PARK<sup>1</sup>, WAN KIM<sup>1</sup>, EUN-JI KIM<sup>1</sup>, SANG-EUN BAE<sup>2</sup>, JONG-YUN KIM<sup>2</sup> and HEON-CHEOL SHIN<sup>1,\*</sup>

<sup>1</sup>School of Materials Science and Engineering, Pusan National University, San30, Jangjeon-dong, Geumjeong-gu, Busan 609-735, Republic of Korea

<sup>2</sup>Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute, Dukjin-dong 150-1, Yuseong-gu, Daejeon 305-353, Republic of Korea

\*Corresponding author: Fax: +82 42 5144457; E-mail: hcshin@pusan.ac.kr

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A variety of rough tungsten electrodes were created and their surface morphology and apparent electrochemical reactivity were analyzed, in order to explore their feasibility as a highly reactive working electrode in electrochemical cells. For this purpose, tungsten electrodes with different surface irregularities were prepared by a chemical etching process and the self-similar fractal dimensions of their surfaces were determined. Then, the integrated charges for hydrogen evolution on their surfaces were estimated in the potentiostatic condition as a measure of their surface reactivity.

**Key Words:** Tungsten, Roughness, Fractal, Surface reactivity, Hydrogen evolution.

### INTRODUCTION

Electrochemical analysis has been considered as an important means to study actinide-related reactions in high-temperature molten salt<sup>1,2</sup>. One of its critical issues from an environmental perspective is how to obtain reliable experimental data with the smallest possible amount of radioactive species. One promising solution for this is to elevate the surface reaction rate per unit apparent area of the working electrode. Under this concept, the test cell does not have to be modified and higher electrochemical reactivity of the working electrode results in smaller amounts of radioactive species needed in the molten salt for a reliable measurement. Making the electrode surface geometrically rough would be the most effective way to increase the areal electrochemical reactivity (*i.e.*, current density). However, it is not so easy to control the surface roughness or porosity of metals such as molybdenum and tungsten used as the working electrode in molten salt. Although the chemical etchant of tungsten is known for its use in surface cleaning<sup>3-5</sup>, the dependence of the surface roughness on the etching conditions has not been systematically studied.

In this work, a variety of rough tungsten electrodes were created by chemical etching and their surface morphology and electrochemical reactivity were analyzed, in order to find the governing factors that control their morphology and to study their possible use as highly reactive electrodes in electrochemical

cells. For this purpose, tungsten electrodes with different surface irregularities were prepared by a wet chemical method from hydrogen peroxide solution as a chemical etchant<sup>3,5</sup> and their surface morphologies were quantitatively analyzed on the basis of fractal geometry. After that, the integrated charges for hydrogen evolution on their surfaces were determined by applying constant potential to evaluate their electrochemical reactivity. Finally, the qualitative relationship between fractal dimension and electrochemical reactivity is discussed.

### EXPERIMENTAL

**Preparation of tungsten electrodes with different surface morphologies:** The as-received tungsten foil (Alfa Aesar, 99.95 %) was chemically etched for 10 min in an aqueous solution of 30 % potassium hydroxide (KOH) by volume at 50 °C in order to remove the native oxide film. The resulting sample had a mirror-like surface to the naked eye and the compositional analysis of its surface by energy-dispersive X-ray spectrometry (EMAX, 7593-H, Horiba, Japan) proves that the native oxide was completely removed. The pre-treated sample with mirror-like surface is called the standard sample hereafter.

The etching solution was prepared by mixing an aqueous hydrogen peroxide solution (H<sub>2</sub>O<sub>2</sub>, 50 %, Aldrich) with deionized water. Three etching parameters-the etchant (H<sub>2</sub>O<sub>2</sub>) content, etching time and temperature-were selected as possible factors affecting the surface morphology of etched samples. First, the

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effect of  $\text{H}_2\text{O}_2$  content and etching time on the surface morphology was analyzed with tungsten samples etched for 10 and 20 min at 80 °C (this is the usual cleaning temperature for tungsten surfaces) in  $\text{H}_2\text{O}_2$  concentrations ranging from 10 to 50 % by volume. The temperature effect was investigated for the samples etched at the solution temperature range of 25 to 80 °C for 20 min in the 30 %  $\text{H}_2\text{O}_2$  solution. The surface morphology of the standard and etched samples was examined by field-emission scanning electron microscope (Field-Emission SEM, S-4800, Hitachi, Japan) and atomic force microscope (AFM, XE-120, Park Systems, South Korea).

**Electrochemical tests for chemically roughened tungsten electrodes:** The electrochemical reactivity of the chemically etched, rough tungsten surface was evaluated by the integrated charge during cathodic hydrogen evolution in the potentiostatic condition. For this purpose, the standard samples with well-defined projected surface areas of 0.5 and 1  $\text{cm}^2$  were first prepared and the amounts of charge passed during the hydrogen reduction reaction were measured for 100 s at -0.1 V vs. SCE in a 0.1 M aqueous solution of sulfuric acid ( $\text{H}_2\text{SO}_4$ , Ducksan, Korea), to verify whether the integrated charge for the hydrogen reduction process reflects the electrochemically active area of the porous tungsten electrode. Then, the integrated charges of the chemically etched tungsten electrodes with various surface morphologies were investigated in the same manner as the standard sample.

## RESULTS AND DISCUSSION

### Change in surface morphology with etching conditions:

The effect of  $\text{H}_2\text{O}_2$  content in 80 °C etching solution on the surface morphology of tungsten is shown in Fig. 1. The standard sample had virtually no notable irregularity on the microscopic image (Fig. 1a), while the chemically etched tungsten surfaces were quite uneven. The etched surface was characterized by terraced structure with severe micro-to nano-sized roughness.

It appeared that the terraced structure became much clearer and the lateral/vertical undulations grew to be wider/deeper in the solution with higher  $\text{H}_2\text{O}_2$  content (Figs. 1b-d) and longer

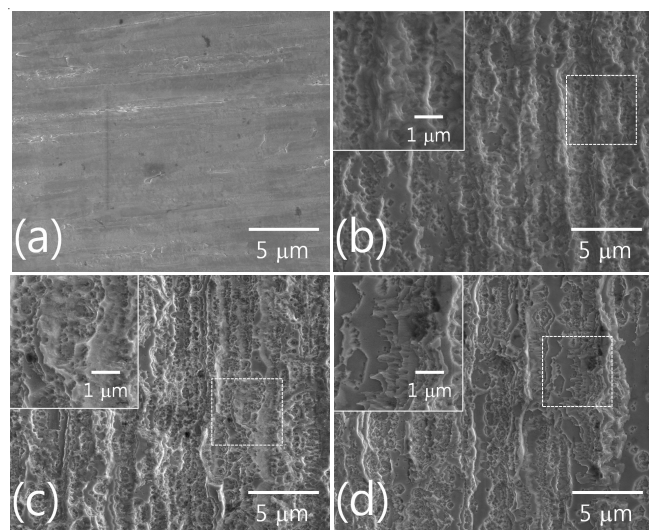


Fig. 1. Surface views of (a) tungsten standard sample and (b)-(d) the samples etched for 10 min. in 80 °C aqueous solutions with different  $\text{H}_2\text{O}_2$  contents: (b) 10; (c) 30; (d) 50 %

etching time (Fig. 2). Notably, the roughest surface was not created in the highest 50 %  $\text{H}_2\text{O}_2$  concentration (Fig. 2c), but rather in the intermediate 30 %  $\text{H}_2\text{O}_2$  concentration (Fig. 2b). There were many flat regions on the tungsten surface etched for 10 min in 50 %  $\text{H}_2\text{O}_2$  solution (Fig. 1c). Longer etching time caused only somewhat higher surface unevenness (Fig. 2c). Due to the complexity of the porous structure, further useful comparative discussion on the morphology of the etched surfaces regarding etching time and  $\text{H}_2\text{O}_2$  content was not possible. The surface morphologies of the samples treated in 20 and 40 %  $\text{H}_2\text{O}_2$  solutions were not suggested in this work because there was nothing worthy of consideration, as shown in Fig. 4.

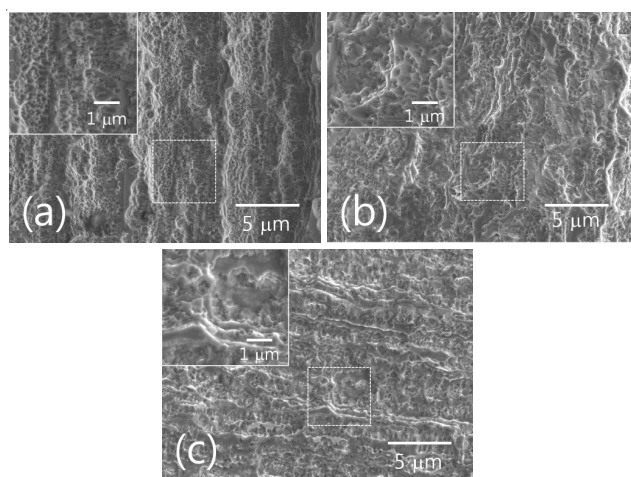


Fig. 2. Surface views of tungsten samples etched for 20 min. in 80 °C aqueous solutions with different  $\text{H}_2\text{O}_2$  contents: (a) 10; (b) 30; (c) 50 %

The surface morphologies of tungsten samples treated at different temperatures of etching solution are shown in Fig. 3. The portion of the smooth area that did not appear to be seriously affected by the etchant decreased with elevating solution temperature (see the stripe-shaped regions in the insets of the figures), manifesting that the chemical etching of tungsten by  $\text{H}_2\text{O}_2$  solution is a usual thermal activation process. The striped pattern was even found on the surface etched in the 60 °C  $\text{H}_2\text{O}_2$  solution, but it completely disappeared in the 80 °C solution. This implies that the temperature of  $\text{H}_2\text{O}_2$  solution needs to be at least 80 °C to obtain uniform surface roughness.

**Quantification of surface irregularity based on fractal geometry:** The root mean square (RMS) roughness has long been used for the quantitative analysis of surface morphology. However, the RMS value is improper for use in our case, because it only describes the height variations in the surface and gives no information about the three-dimensional (3D) surface irregularity that the electro-active species in the electrolyte actually sense during the redox processes. In this work, the morphology of the tungsten surface was analyzed on the basis of fractal geometry. Specifically, the self-similar fractal dimension  $D_f$  which reflects the 3D surface asperities was determined for the standard and etched tungsten samples by a triangulation method shown below<sup>6</sup>. The surface morphology of the samples was analyzed using an atomic force microscope to obtain a set of (x,y,z) points on the surface. The

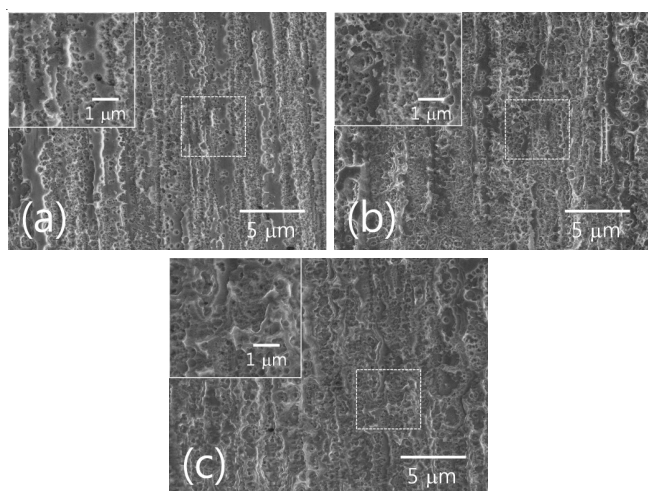


Fig. 3. Surface views of tungsten samples etched for 20 min. in 30 %  $\text{H}_2\text{O}_2$  containing solutions of different temperatures: (a) 25; (b) 40; (c) 60 °C

(x, y) plane with an area of  $L^2$  is divided into  $N^2$  equal segments and the surface is covered by the resulting  $2N^2$  triangles with projected triangle size (PTS) of  $L/N$ . The scaled surface area (SSA) for each PTS is determined by the summation of the areas of all triangles. Then, based on the fractal theory, the self-similar fractal dimension ( $D_f$ ) of the surface is given by  $2-d \log \text{SSA}/d \log \text{PTS}$ .

Scaled surface area values for various PTSs were determined at the roughened tungsten samples by applying a triangulation method to their atomic force microscope images (not presented in this work). The resulting PTS vs. SSA plots are given in a logarithmic scale in Fig. 4, together with the self-similar fractal dimensions  $D_f$  calculated from the linear relationship between log SSA and log PTS. The tungsten samples etched for 10 min were characterized by similar  $D_f$  values ranging from 2.010 to 2.015, irrespective of the  $\text{H}_2\text{O}_2$  content in the etching solution (Fig. 4a), while the tungsten surfaces etched for 20 min in the solutions containing 20 and 30 %  $\text{H}_2\text{O}_2$  showed much higher values of  $D_f$  than the surfaces treated in the solutions with other  $\text{H}_2\text{O}_2$  contents (Fig. 4b). In particular, the 30 %  $\text{H}_2\text{O}_2$  etching solution resulted in the highest  $D_f$  value of 2.040, which is consistent with the microscopic observation that the roughest surface is created in the 30 %  $\text{H}_2\text{O}_2$  concentration, as explained in Fig. 2. In addition, there is great consistency between the microscopic images (Fig. 3) and  $D_f$  values (Fig. 4c) in the tungsten samples treated at different etching temperatures. The sample etched at 80 °C showed the roughest surface and the highest  $D_f$ . This strongly indicates that the self-similar fractal dimension reflects the 3D surface irregularity of the chemically etched tungsten electrode quite well.

**Electrochemical reactivity of chemically roughened tungsten electrodes:** Hydrogen gas was cathodically generated on the tungsten surfaces under potentiostatic condition in order to evaluate their electrochemical reactivity (or electrochemically active surface area). Before the experiments on the roughened samples, the standard samples with well-defined projected surface areas were tested to verify whether this method is relevant for estimating the surface reactivity. It is proven that the ratio of the currents (Fig. 5a) together with the resulting rates of integrated charge increase (Fig. 5b) in the

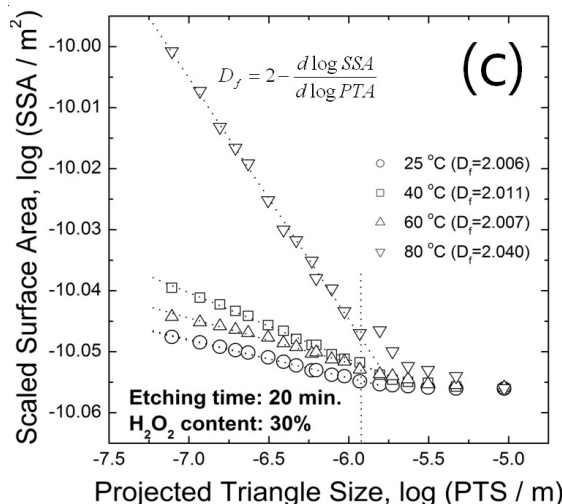
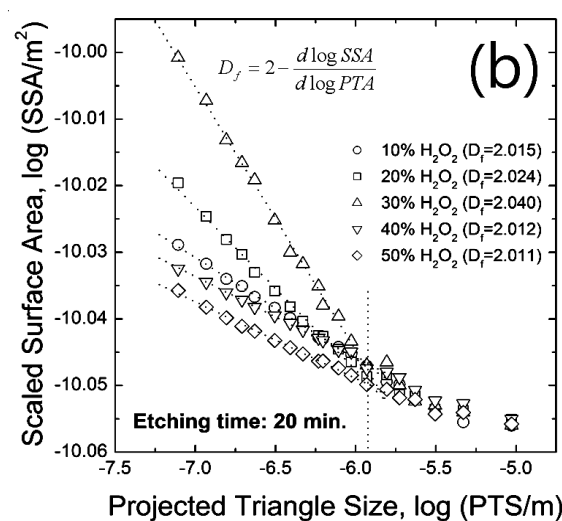
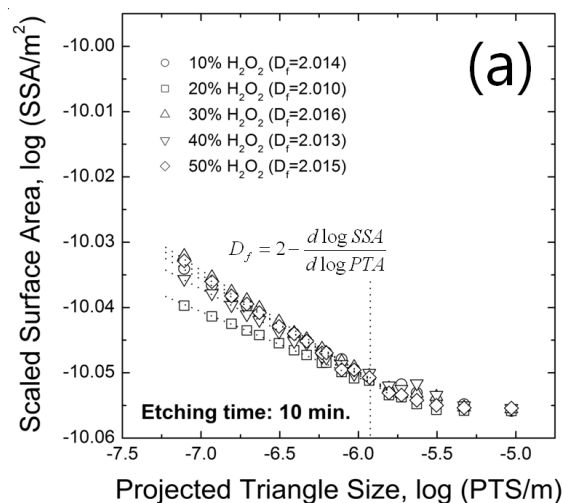


Fig. 4. Projected triangle size vs. scaled surface area plots for the samples presented in (a) Fig. 1, (b) Fig. 2 and (c) Fig. 3. Fractal dimensions  $D_f$  were suggested in the figures

steady-state region coincided quite well with the ratio of projected surface areas of the standard samples. This implies that the current or the increase rate of integrated charge during hydrogen reduction in the potentiostatic condition can be effectively used to analyze the relative electrochemical reactivity of roughened tungsten samples.



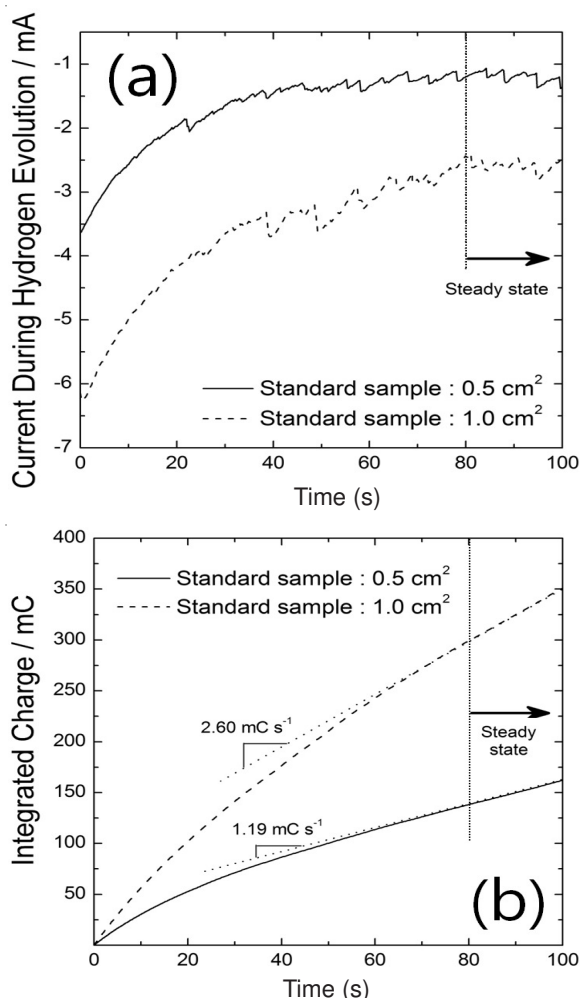


Fig. 5. (a) Current transients and (b) resulting integrated charge transients of standard samples with different surface areas during potentiostatic hydrogen generation

Figs. 6a and b show the cathodic current transients and the resulting integrated charge transients, respectively, of the tungsten samples etched for 20 min in the solutions with different  $\text{H}_2\text{O}_2$  content, determined in the course of hydrogen evolution in the potentiostatic condition. The current densities or the increase rates of the integrated charge densities of the roughened tungsten electrodes were more than two times higher than that of the standard sample, with a surface area of  $1 \text{ cm}^2$ , implying that the roughened samples have much higher apparent electrochemical reactivity for hydrogen reduction. In addition, the current and the charge increase rate of the sample etched in 30 %  $\text{H}_2\text{O}_2$  solution were the highest, followed by the corresponding values of the sample treated in 20 %  $\text{H}_2\text{O}_2$  solution. This shows remarkable consistency with the result of the self-similar fractal dimension (Fig. 4b). This indicates that the fractal dimension might be a reliable measure of the electrochemically active surface area or surface reactivity of roughened tungsten electrodes.

### Conclusion

Tungsten electrodes with different surface roughnesses were fabricated by a chemical etching process and their self-

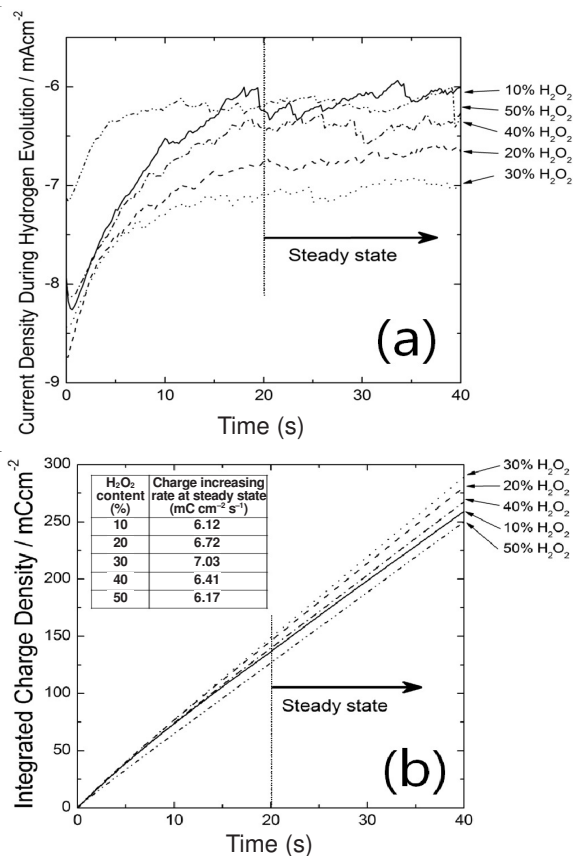


Fig. 6. (a) Current transients and (b) resulting integrated charge transients of tungsten samples suggested in Figs. 2 and 4(b) during potentiostatic hydrogen generation

similar fractal dimensions and electrochemical reactivity were analyzed. The fractal dimension reflected both the surface irregularity and the electrochemical reactivity of the chemically roughened tungsten samples quite well. The rate of hydrogen reduction reaction on the roughened samples was more than two times faster than that on the smooth sample.

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