Development of a Software to Analyze the Dispersion State of Particles on a Flat Substrate

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A program called “Roughness Analyzer,” has been developed with Visual Basic Language, and it can analyze the dispersion state of particles on a flat substrate from a three dimensional profile obtained by surface roughness meters. This software enables us to separate secondary particles agglomerated on the substrate to calculate the area, the volume and the average height of each secondary particle. Further, the surface of the substrate can be divided into any number from the center of the substrate in a radial direction and an angular direction, and then it is possible to calculate the area, the volume and the area occupied by the particles in each section. In addition, this software has functions such as the correction of only the shape of the substrate by a spline interpolation method and the conversion of any range on the substrate surface to DXF format.

Keywords: Roughness Analyzer, Dispersion state, Secondary particles, Cluster analysis, Height data

1 INTRODUCTION

Functional particles such as TiO\textsubscript{2} and Pt/C are often fixed on a flat substrate for practical uses. For example, a rotating ring disk electrode (RRDE) technique, in which Pt/C nanoparticles were dispersed on a glassy-carbon (GC) disk electrode, is known as a method capable of evaluating the activity of catalysts. The technique was often applied to the evaluation of oxygen reduction catalysts used in fuel cells or metal-air batteries, because the reaction intermediates such as hydrogen peroxide can be detected by the ring electrode [1,2]. However, the accuracy of the technique was significantly affected by the dispersivity of the catalyst particles on the electrode [3,4]. Thus, the catalysts on the disk electrode are required to be uniformly dispersed, and many researchers have sought the best distribution method. Uchida et al. reported that the best dispersion for the carbon black supported platinum nanoparticles was achieved by using ethanol for the catalyst suspension, followed by the evaporation of the suspension droplet on the GC slowly under the saturated vapor pressure of ethanol [3].

Although microscope photographic images are used for the estimation of dispersivity on the electrode, no quantitative analyses were performed by using the images. This is because it is difficult to obtain the dispersiveness of the particles on the electrode by using software packages for general image analysis such as “ImageJ” [5] with photographs or height data. Furthermore, a software package for the analysis of particle distribution on a substrate has not been reported generally.

In this study, we have developed a program called “Roughness Analyzer” which can quantitatively analyze the dispersiveness of particles on a flat substrate from a three dimensional profile using Visual Basic.NET\textsuperscript{®} 2013. The Roughness Analyzer can determine the respective area and volume of each secondary particle composed of the catalysts. Moreover, the software is equipped with a function for the estimation of a substrate surface by a spline interpolation method.

2 FEATURE OF ROUGHNESS ANALYZER

Figure 1 shows the control panel of the Roughness Analyzer. This software can load the three dimensional data of particles fixed on a substrate measured by a surface roughness meter (SV-C4500 CNC, Mitutoyo) as well as the data of other devices by copying the data of a tab-delimited contour map type format to a clipboard. Please refer to this software documentation for more information. The information of loaded data is shown in the information table (Figure 1 (a)). Figure 1 (b) is the 2D contour map of the loaded data and the height of each point is expressed by the brightness of each dot. If necessary, a user can change the range of height represented by the brightness and the number of levels (Figure 1 (c)). It should be noted that, there are three “Tab pages” that display visualization images. “Channel 0” shows experimental raw data. “Channel 1” displays only a substrate shape which is inferred by a cubic spline interpolation method. Then the height of only particles on the substrate is displayed in “Channel 2” by subtracting the height of channel 1 from that of channel 0 (Figure 1 (d)).

Table 1 shows the commands of “Roughness Analyzer” allocated to the menu bar. The important functions in the menus for the analysis are described below.

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2.1 Tools menu

Figure 2 shows a “Create Base Geometry” form module displayed by [Tools] – [Create Base Geometry]. In the module, only a substrate surface can be estimated from the three-dimensional data of the particles fixed on a substrate. First, when a user clicks a “Detect” button, an analytical range is automatically determined. It should be noted that the analytical range is detected by scanning in the horizontal direction of the visualization image and both ends of an analytical range are displayed in red points respectively (Figure 2 (a)). The red curve in Figure 2 (b) means a cross-section at a horizontal yellow line on the visualization image. Next, the user determines the number of points on the baseline in the cross section curve and clicks a “Create” button. Then, local minimum points (green points in Figure 2 (b)) are adopted as initial surface points of the substrate, and a curve connecting these points is calculated by a spline interpolation method (blue line in Figure 2 (b)). In addition, the green points can be moved by dragging, and the spline curve is recalculated automatically. Thus, the user can estimate the substrate surface more accurately. Finally, the estimated substrate surface is displayed at “channel 1” tab in the control panel window by clicking a “Apply to Ch1” button, and then only particle-derived height data are calculated by subtracting the height of the channel 1 from that of channel 0 by pushing a “Calc” button (Figure 1 (d)).

2.2 Calculation menu

Figure 3 shows a “Cluster Analysis” form module displayed by [Tools] – [Cluster Analysis]. The functions equipped with this module are “Cluster Analysis” and “Distribution Analysis.” The “Cluster Analysis” can detect each secondary particle agglomerated on the substrate and can analyze the area, the volume and the average height of each secondary particle (Figure 3 (a)). This function is implemented by a modified scan-line seed fill algorithm [6] as follows: Local maximum points are determined by scanning both in the horizontal and vertical direction of the particle-derived height data, and then a secondary particle started to be defined from the highest local maximum point. A region surrounding to the threshold of height is considered a secondary particle. Each secondary particle is filled with a different color. The area, the volume, and the average height of each particle are calculated respectively. It should be noted that the local maximum points included in the already analyzed secondary particles are excluded from the start points of the modified scan-line seed fill method.

The “Distribution Analysis” can divide the substrate surface into any number from the center of the substrate surface in a radial direction and an angular direction (Figure 3 (b)). Further, it can automatically calculate the area, the volume and the percentages...
of area occupied by particles in each section. The user can choose a split style in the radial direction (“Same interval” mode in which the intervals are equal in length or “Same area” mode in which the area of each section is constant). Note that, the accuracy of these analyses is derived from the measurement accuracy of three-dimensional data.

3 APPLICATION TO A MODIFIED ELECTRODE

For example, the dispersiveness of a modified GC electrode was evaluated by the software. The electrode was prepared as follows: A 2.0 mg of Pt/MWCNTs was suspended in 1 mL of 0.1 wt% Nafion-MeOH or Nafion-EtOH by ultrasonication for 10 min. Then, 10 µL of the suspension was cast onto a GC disk (6 mm φ, 0.283 cm²) – Pt ring electrode (Nikko Keisoku) and dried for 1 h at R.T.

Figure 4 (a) shows the visualization images for secondary particles on a GC disk electrode. The secondary clusters using MeOH were larger than those using EtOH. For the distribution analysis, the radius and angular of the GC surface were divided into 10 parts, respectively, to produce 100 parts with the same area.

Figure 4 (b) shows the normalized cumulative distribution of the volume of each cluster. When a lot of small secondary particles exist on the surface such as in the case with EtOH as a solvent, the curve rises steeply to reach a plateau, whereas when large clusters exist, the curve rises gradually. The analysis enables us to evaluate the reproducibility of the secondary cluster size. Furthermore, it might be possible to evaluate the reproducibility of the amount of the catalysts with a high resolution device such as a scanning tunnel microscope.

Figure 4 (c) shows the relationship between the average heights of the secondary particles and the logarithm of cluster area. In both cases, the average heights of the secondary particles increased steeply to reach a plateau. The analysis enables us to evaluate the reproducibility of the secondary and the logarithm of cluster area, (d) Percentages of area occupancy for the secondary particles in each section.

Figure 4. Analysis results of Pt/C on a GC disk electrode by Roughness Analyzer. (a) Visualization images for secondary particles on a GC disk electrode. (b) Normalized cumulative distribution of the volume of the cluster, (c) Relationship between the average height of each secondary particle and the logarithm of cluster area, (d) Percentages of area occupancy for the secondary particles in each section.
with increase in the logarithm of cluster areas in the same way, suggesting that the average height and the volume of a secondary particle can be estimated on the basis of a cluster area obtained from a two-dimensional microscope image of the substrate as well as three-dimensional data measured by a surface roughness meter. Figure 4 (d) shows the percentage of the area occupancy for the secondary particles in each section shown in Figure 4 (a). Each cumulative bar represents the percentage of area occupancy in the same radial range, thus, it means good dispersivity of the particles when each cumulative bar has similar height, namely, the standard deviation of the heights is small. Moreover, each element in each cumulative bar means the percentage of area occupancy for the particles at a different angular direction in the same radial range. The desirable dispersivity can be achieved when the standard deviation of the height of the bars is small. However, the small standard deviations are not a sufficient condition for good dispersivity. Criteria for dispersivity are the average height of the particles as well as the standard deviations. In this case, the parameters using EtOH as a solvent were better than those using MeOH (Table 2).

### Table 2. Standard deviations of the area occupancy for the secondary particles in the radial and angular direction, and the average height of the secondary particles consisting of Pt/MWCNTs.

| Solvent | S.D. | Average height |
|---------|------|----------------|
|         | Radial direction | Angular direction |
| MeOH    | 0.155 | 0.259 | 6.2 |
| EtOH    | 0.153 | 0.209 | 5.0 |

4 CONCLUSION

We have developed a software called “Roughness Analyzer” which can quantitatively analyze a dispersion state of particles on a flat substrate from a three dimensional data measured by a surface roughness meter. This software is equipped with two analytical functions, namely the Cluster Analysis that enables us to calculate the area, the volume and the average height of each particle, and the Distribution Analysis that can determine the dispersion state of the particles in radial and angular directions. Further, this software is equipped with a function for the estimation of a substrate surface by a spline interpolation method.

5 AGREEMENTS FOR USING THE PROGRAM

The “Roughness Analyzer” is freeware and executable on Windows Vista/7/8.1/10 with .Net framework 4.5.

We cannot be responsible for damages that you might receive using this program. Please feel free to contact us, when you find bugs. We would welcome suggestions for the improvement of the program. The program can be downloaded at https://xythos.tokyo-ct.ac.jp/web/c/hshiroyoshi/freeware.htm.

REFERENCES

[1] K. Oyaizu, M. Yuasa, et al., Electrochemistry, 73, 1060 (2005).
[2] K. Oyaizu, M. Yuasa, et al., Electrochemistry, 74, 81 (2006). [CrossRef]
[3] E. Higuchi, H. Uchida, et al., J. Electroanal. Chem., 583, 69 (2005). [CrossRef]
[4] M. Inaba, et al., Electrochem. Solid-State Lett., 7, A474 (2004). [CrossRef]
[5] W. S. Rasband, J. Image, U. S. National Institutes of Health, Bethesda, Maryland, USA, http://rsb.info.nih.gov/ij/, 1997–2012.
[6] AR. Smith, Comput. Graph., 13, 276 (1979). [CrossRef]