Improvement of the inter-electrode reproducibility of screen-printed carbon electrodes by oxygen plasma etching and an image color level method for quality control

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ABSTRACT

Screen-printed carbon electrodes (SPCEs) were selectively etched by oxygen plasma. The coefficient of variance (CV) of inter-electrode reproducibility was reduced from 21.6 to 4.6. Studies of the surface by color-level-indexing histogram analysis, scanning electronic microscopy (SEM) and resistance revealed that the inter-electrode reproducibility correlated with complete etching of the resin binder from the SPCE surface. The quality of the electrode was differentiated by this color level index analysis. This technique has great potential for application in on-line quality control of the SPCE plasma-treating process when integrated with suitable image processing software.

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1. Introduction

Screen-printed carbon electrodes (SPCEs) are widely used in the fabrication of both chemical and biochemical sensors for on-site biomedical diagnosis and industrial applications [1–5]. SPCEs exhibit many attractive properties including low-cost, versatility and particularly the possibility of mass production [6,7]. Because the surfaces of commercialized SPCEs are largely covered by organic oil, graphite, and pasting binder (e.g., polyester resin, ethyl cellulose, or vinyl or epoxy-based polymeric binder and/or other pollutants), the electrode-to-electrode reproducibility of SPCEs is significantly affected by the manufacturing process and the formulation of printing inks. Several methods have been proposed to improve the electrochemical properties and sensitivity of carbon-based electrodes, including pre-anodization [2], electrochemical cycling [8], metal-dispersion [9–11], soaking [12], and electrochemical metallization [13]. The enhancement in response is due to the removal of organic ink constituents, thereby increasing surface roughness and/or functionalities [12]. However, the methods described above were unable to remove the binder, which was used to increase the viscosity of the ink in the printing process, from the SPCE surface completely and did not

demonstrate appreciable improvement of electrode-to-electrode reproducibility [7]. Plasma treatment has many advantages over other surface modification technologies, such as requirement for fewer reagents, lower environmental pollution and near-ambient procedural temperatures. It is frequently used to clean and modify the surfaces of materials, including graphite [13–16], glass [17], glassy carbon [18] and plastic substrates, such as polyimide, polymethamethylacrylate, poly(dimethylsiloxane) and SPCEs [19,20]. However, SPCEs are a composite mixture made of graphite, solvent, pasting binder and other additives [14,21]. Resin is added to the mixture just prior to screen-printing. It has been reported that smoother electrodic surfaces are usually obtained when SPCEs are exposed at lower curing temperatures due to the lower evaporation rate of the solvent. This is attributable to the generation and lumping together of particles with smaller sizes on the SPCE surface [19,20]. The lumped particles and the binder tend to fill the surface holes between graphite particles resulting in low electron transfer rates [19,20] and poor electrode to electrode reproducibility. The surface characteristics of plasma treated graphite particles have been widely discussed in previous reports. Cascarini et al. [14] found that oxygen plasma could smoothly peel off the outer layer of graphite without damaging the graphite. Takada et al. [15] reported that carbon black could be gradually etched off after exposure to oxygen plasma (power 20 W) for more than 20 min. For SPCE, unlike free graphite, the graphite as well as the additive adheres to the surface of the plastic strip through the action of the

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resin binder. Although the surface characteristics of argon plasma-treated SPCEs have been investigated [19,20], data is comparatively limited on the dynamic change and inter-electrode reproducibility of the plasma treated SPCEs. Unlike argon plasma, the oxygen plasma not only sputters the SPCE surface but also causes a chemical reaction and produces heat on the SPCE surface. The resin binder polymer was removed by oxygen plasma and heat significantly affected the properties of SPCEs including electron transfer rate and electrocatalytic activity [22]. A technology called "selective plasma etching", which uses a weakly ionized oxygen plasma created by a RF generator of a lower output power, can be employed to perform selective etching of resin polymers. This technology is based on the phenomena that different types of polymers can be etched at different rates [22] and is commonly used in the chemical industry as a method of sample preparation prior to scanning electron microscope (SEM) analysis to profile the particle size distribution in polymer matrix [23].

This study investigated the dynamic changes in the surface structure of SPCEs induced by oxygen plasma etching including electrochemical responses, surface capacitance, surface topology, and both the intra-electrode and electrode-to-electrode (inter-electrode) reproducibility. In addition, a method based on the color level index to evaluate the surface of etched SPCEs is presented. Our results indicate that this method has great potential for applications in on-line quality control of the SPCE plasma-treatment process.

2. Experimental

2.1. Reagents

The SPCE has a rectangular form with both the working and counter electrodes positioning on the same surface area of 4.8 mm^2 and printed using heat curing carbon composite inks. These strips are printed onto a plastic substrate and an insulating layer serves to delimit a working area and electric contacts. Ink formulation and production characteristics of commercial SPCEs are regarded by the manufacturers as proprietary information. The assay buffer was 1× phosphate buffer saline (PBS). Hydrogen peroxide (30%) was obtained from Sigma (St. Louis, MO, USA). Other chemicals used were of analytical grade. All solutions were prepared with deionized distilled water (d.d. H$_2$O).

2.2. Oxygen plasma treatment

Oxygen plasma treatment was performed in a 13.56-MHz radio frequency (RF) plasma reactor designed by Branchy Technology Co. Ltd. (Tao-Yuan, Taiwan). The reactor was first evacuated to a base pressure of less than 10^{-3} Pa before the plasma gas was introduced. All of the procedures were performed at room temperature.

The SPCE was then placed in the center of the reactor and exposed to oxygen plasma in the RF plasma reactor under a constant system pressure of 13 Pa at a flow rate of 10 m/s. The oxygen plasma treatment of the SPCE was performed at plasma powers of 100, 200 and 300 W, respectively, for different lengths of time at 0, 5, 10, 15, 20 and 25 min, respectively.

2.3. Optical micrographs and scanning electronic microscopy

The optical micrographs of SPCE surfaces with 50× magnification were obtained using an Olympus BX51 microscope with a DP12 digital camera. Scanning electronic microscope (SEM) images were taken with a Hitachi S-2400 (Angstrom Scientific Inc., NJ, USA) at the College of Life Science of National Taiwan University with magnifications of 500× and 7000×. The light sources for the optical microscopy and SEM were controlled at the same light intensity levels.

2.4. Surface resistance measurements

Surface resistances of the SPCEs were measured using a surface resistivity meter (BHO-385, Taipei, Taiwan). The probe of the meter was placed on flat spots of the SPCEs and data were displayed on an analogue meter to determine the surface resistance. Measurements were performed at four different random positions of the same electrode.

2.5. Electrochemical measurements

Cyclic voltammetric and amperometric measurements were performed using an electrochemical analyzer (model CHI 440, West Lafayette IN, USA). All experiments were performed using a conventional three-electrode system, with an Ag/AgCl electrode as the reference electrode. Input and output signals from the potentiostat were coupled to a personal computer (1.8 GHz Pentium microprocessor). The cyclic voltammetric measurements of electrodes were performed in a phosphate buffer (100 mM, pH 7.0) without stirring. The scanning rate for cyclic voltammetry was 50 mV/s. The resulting cyclic voltammogram was used to calculate the surface capacitance using the method described by Okajima et al. [24].

The amperometric measurements were performed by adding 0.1 mL of hydrogen peroxide into a cylindrical cell with 9.9 mL of PBS buffer (pH 7.0) under a fixed potential of 0.5 V vs. the Ag/AgCl electrode. Unless otherwise stated, all experiments were performed at 37 °C. The baseline current was achieved prior to injection of the test solution. Magnetic stirring during the operation was used to ensure the homogeneity of the solution. The response current was defined as the difference between the baseline and the steady-state current.

2.6. Color level index analysis

The SPCE surface was photographed at 0, 5, 10, 15, 20, and 25 min after oxygen plasma treatment with an optical microscope at a magnification of 50×. At each time frame, 3 randomly selected areas were photographed and used as replicates. The optical micrographs of SPCE surfaces were then converted to digital black-and-white image data files by PhotoImpact 7.0 (Ulead System, Taipei, Taiwan). The pixels of each image file were then categorized in the form of a histogram according to their respective color standings in the 256 gray scale by the same software, using the x-axis for the color scale and the y-axis for the number of pixels. The percentage of pixels of each color level could be presented by PhotoImpact 7.0. We choose the color level of 45 as the black color and 170 as the white color cut off level. The color-level-indexing histograms from different time frames were then compared to determine the effect of oxygen plasma treatment on SPCE surfaces. For each time frame, the frequency distributions of 3 replicates were averaged for statistical analysis. The percentages of black colors (0–45) and white colors (170–255) at different treatment times were then compared and checked to determine the effect of oxygen plasma according to the results of statistical analysis.

3. Results and discussions

3.1. Reproducibility of oxygen plasma-treated SPCEs

Five SPCEs were randomly selected and treated with oxygen plasma at 100 W power for 0, 5, 10, 15, and 20 min and then immersed in a 9.9 mL phosphate buffer solution (100 mM, pH7.0) with temperature controlled at 37 °C. Then, a microsyringe was used to inject 0.1 mL of H$_2$O$_2$ solution into the test solution. The currents across the electrodes were measured when the oxidation of H$_2$O$_2$ took place. The effects of oxygen plasma treatment on the electrochemical reactivity of SPCEs for the oxidation of H$_2$O$_2$ are shown in Table 1. The

Table 1
Effects of oxygen plasma treatment on the electrochemical reactivity of the SPCEs to H_2O_2. The oxygen plasma was carried out under a power of 100 W for the indicated treatment times.

Treatment time (min)	Intra-electrode averaged response (nA)[a] (mean ± S.D.)	CV (%)	Inter-electrode averaged response (nA)[b] (mean ± S.D.)	CV (%)
0	4.60 ± 1.04	22.6	4.07 ± 0.88	21.62
5	81.9 ± 16.6	20.3	89.19 ± 31.94	35.8
10	159.0 ± 29.6	18.6	159.81 ± 16.01	10.0
15	352.3 ± 10.5	3.0	325.45 ± 68.84	21.2
20	333.7 ± 16.0	4.8	343.62 ± 15.97	4.6

[a] The data represent the average valves of three measurements from the same electrode.
[b] The data represent the average valves of 15 measurements from five-independent electrodes.

average of 3 measurements of oxidative currents from the same SPCE, or intra-electrode responses, is shown in the second column and the average of 15 measurements from those 5 independent SPCEs, or inter-electrode responses, is shown in the fourth column of Table 1. The response increased rapidly at a rate of 23 nA/min during the initial 15 min and then increased slowly afterwards at a rate of 2.8 nA/min only. Although extended plasma treatment time had a limited effect on the enhancement in current response, it was essential to the improvement of both inter-electrode and intra-electrode reproducibilities. The intra-electrode and inter-electrode reproducibilities (CV) are shown in the third and fifth columns of Table 1, respectively. Both reproducibilities improved significantly after treatment for 20 min. The inter-electrode CV reduced from 21.6% at minute 0 to 4.6% at minute 20, while the intra-electrode CV decreased from 22.6% to 4.8% during the same time period. These results demonstrate that oxygen plasma treatment is effective in improving the inter-electrode CV.

To explain the improvement of inter-electrode CV after optimal oxygen plasma treatment, the surface capacitance, surface resistance (Fig. 1(b) and (c)) and surface topology vs. plasma treatment time are discussed in Section 3.3.

3.2. Color index analysis

Color index analysis has been used in clinical analysis [25]. In this study, the quality of electrodes was further examined and differentiated using color level index analysis. The optical micrographs of SPCE surfaces are shown in Fig. 2. These micrographs, obtained with the same light intensity level, were converted to black-and-white format and analyzed using the "color level histogram" function of PhotoImpact 7.0. A 256-gray-color scale was used with 0 for pure black and 255 for pure white. The pixels of each image files were categorized in the form of a statistical histogram according to their

respective color standings in the 256 gray scale, using the x-axis for the color scale and the y-axis for the number of pixels.

As shown in Fig. 3 and Table 2, both low-level (e.g. 0–45) and high-level (e.g. 170–255) gray colors decreased gradually when the SPCE was exposed to oxygen plasma treatment. For untreated SPCEs and SPCEs treated for less than 10 min, the histograms were asymmetric and broadly-distributed. By contrast, the histograms of oxygen plasma-treated SPCEs treated for more than 10 min became symmetric and relatively narrowly-distributed as shown in Fig. 3. These findings are consistent with the etching of the binder and removal of the loosened particles from the SPCE. In Table 2, the decrease of white level pixels, e.g. color level >170, may have been due to the disappearance of resin binder from the SPCE surface. As was evidenced by X-ray photoelectron spectroscopy (XPS), after treating the SPCE surface with oxygen plasma, the sp2 sites increase. The result was in agreement with a previous report by other researchers [20], who proposed that the results were due to the binder removal from the SPCE surface. On the other hand, the decrease in black level, e.g. color level <45, was caused by the removal of loosened graphite from the SPCE surface, thereby the contrast of the black and white image decreased, as was evident by the formation of a flat surface on the SEM (data not shown). The reproducibility of the color level index of 3 replicates of different electrode was good with low CV (lower than 5.0%) for each experiment condition. The method only required optical micrograph and a computer. This simple, quick, and inexpensive method may be used to monitor the effect of oxygen plasma treatment on SPCEs.

3.3. Surface topology and physical/chemical properties of oxygen plasma treated SPCS

The surface of SPCEs before and after exposure to oxygen plasma was investigated by optical microscopy with a magnification of 50× (Fig. 2) and SEM with a magnification of 7000× (Fig. 4). As shown in Fig. 4(a), the surface of the untreated SPCE was covered with substances comprising pasting binder, graphite particles, solvent, surfactant, and other additives, with a smear-like surface structure. In addition, some small particles, which aggregated loosely on the surface of the electrode, were lumped together by a solvent. The lumped particles were reported to be caused by lower curing temperatures (lower evaporation rate of the solvent) during screen printing [26] and could be related to lower electron transfer rates (4.4 ± 1.0 nA/mM of H_2O_2). Moreover, the lumped particles were unstable on the surface of untreated SPCEs and resulted in poor reproducibility (e.g. intra-electrode CV of 21.8% and inter-electrode CV of 21.6%) as shown in Table 1.

When the SPCE was exposed to oxygen plasma (100 W) the bonding of the lumped particles on the outer layer of the SPCE loosened due to the continuous attack by several free radicals and ions in oxygen plasma [27–30]. These radicals and ions interacted with the
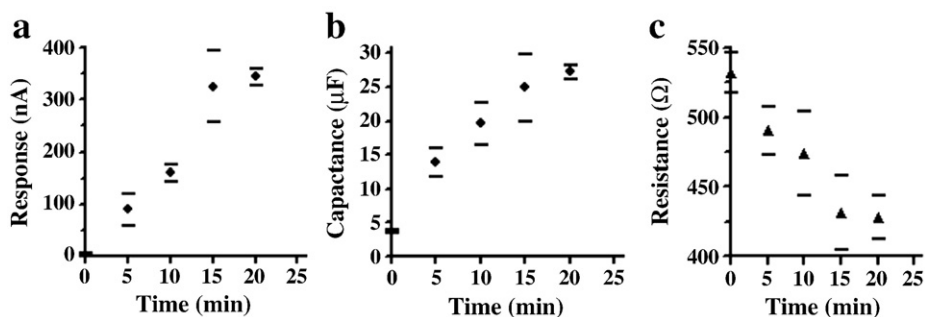

Fig. 1. Effect of oxygen plasma treatment on the formation of oxygenated functionalities of the SPCE. (a) Response of electrode vs. oxygen plasma treatment time, (b) capacitance vs. treatment time, (c) resistance vs. treatment time.
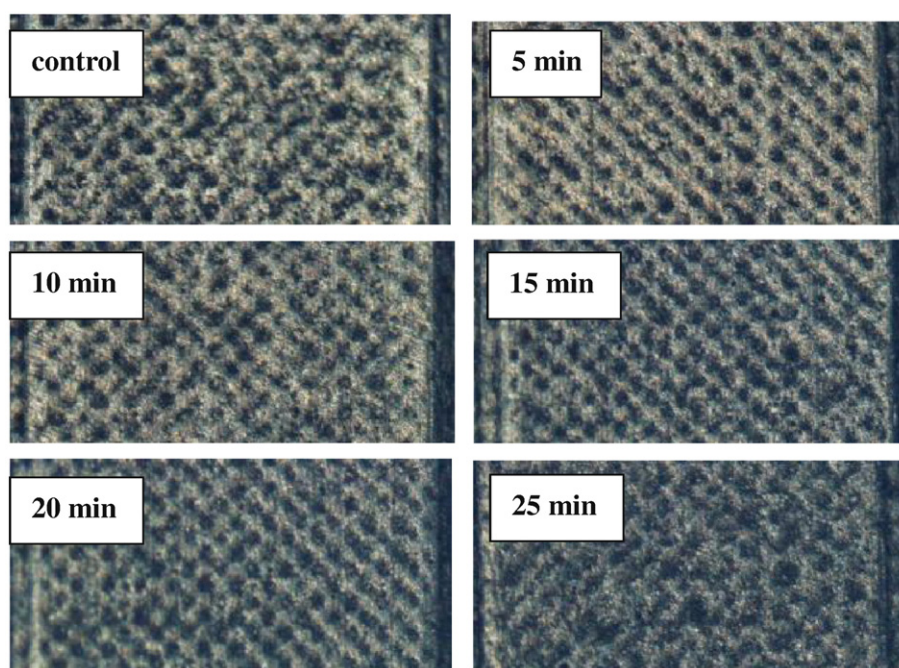
Fig. 2. Optical micrograph images of SPCE, with magnification of 50×, before (control) and after 5, 10, 15, 20, and 25 min, respectively, oxygen plasma treatment.

surface both chemically and physically and generated certain amounts of heat accordingly. The physical effect was bombardment of the surface with ions from the plasma and thus recombination of radicals, whereas the chemical interaction caused oxidation of the surface and generated heat on the surface of the electrode [15]. Since the binding energy (etching efficiency) of the binder and lumped particles were much lower than that of the graphite, the etching rate of the resin was faster than that of the graphite [22]. The resin then interacted with the oxygen plasma introduced on the SPCE surface. The high rate of flux of O atoms on the top of the SPCE removed the resin polymer from the surface. The products resulting from the oxygen plasma reaction, such as CO, CO_2, HO and H_2O, were then desorbed and pumped away. As soon as the resin was removed, the graphite became exposed and was on the SPCE.

After about 5 min of the plasma treatment, the loosely bound particles decomposed into small pieces due to the cumulative physical bombardments. Parts of the pieces were pumped away from the electrode surface by oxygen plasma while others remained on the electrode surface or in the gaps of the graphite particles (Fig. 4b). Fig. 4(b) (within the circle) shows that many small spherical particles and decomposed pieces were packed together on the electrode surface. The image was similar to that of the surface of carbon paste electrodes described by Fanjul-Bolado et al. [26]. The small spherical particles were thought to be the mixture of resin binder and other additives that were employed to enhance the affinity of the ink for the substrate in terms of adhesion properties.

Upon prolonged treatment time, the oxygen plasma caused oxidation of the SPCE surface and resulted in heat generation on the surface and thereby burn-off of the surface binder. During the 10th and 15th minute of oxygen plasma treatment, there was a sharp increase in the current response of the electrode, as shown in Fig. 1(a). We speculated that the sharp increase in current response was due to the removal of the pasting binder which filled in the gaps of graphite particles which covered the surface of the graphite edge planes. Removal of the pasting binder on the SPCE surface could expose the graphite edge planes. This newly exposed graphite surface may provide numerous new edge planes [14,28–35], which have been suggested to be the electrochemically active sites on the graphite particles [30,32,33,36]. This hypothesis is supported by the marked

decrease of electrode resistance during the same period of time as shown in Fig. 1(c). The resulting cyclic voltammogram can be used to calculate the surface capacitance by using the method described by Okajima et al. [24]. However, we only achieved a CV range from 5% to 14% as shown in Fig. 1b. Due to the poor reproducibility, the data were improper for quantitative quality control of SPCEs.

After 15-min of oxygen plasma treatment, the surface temperature could rise substantially above the bulk temperature of the SPCE. Therefore, the small particles were burned off and pumped away from the surface of the electrode (Fig. 3(c)). This was verified by the clean surface of the electrode on the optical microscopic images (Fig. 2).

Because the extension of plasma treatment time to 20 min could completely remove the binder, an excellent inter-electrode reproducibility was obtained. The surface temperature of the electrodes increased with plasma processing time. After 15 min of plasma treatment, the surface temperature of the electrode was exceedingly high. Therefore, as soon as a new layer of resin appeared on the surface of the SPCE, it was etched and removed by the oxygen plasma immediately. Further, the temperature between the gaps of graphite was high enough to remove the binder. The resin binder was almost completely removed after 20 min of plasma exposure (Fig. 3(c)). The reproducibility of the electrode was significantly improved with a low CV (intra-electrode CV = 4.8% and inter-electrode CV = 4.6%), as shown in Table 1. The complete removal of resin binder was also detected by the color level index analysis which showed that the white color level disappeared after 20 min of plasma exposure (Table 2). Our electrodes (as shown in Fig. 2) were fabricated by screen printing, its rough surface makes it difficult to bring into focus for both pits and mounds simultaneously to achieve a good quality of the images. The atomic force microscope (AFM) images should be a better alternative to describe the changes and ideal for the characterization of SPCEs.

Oxygen plasma not only improves the electrocatalytic activity of SPCEs to H_2O_2 as described above but also improves the electrochemical properties of SPCEs. The electron transfer kinetics of the plasma-treated SPCEs was investigated by measuring the cyclic voltammetric behavior of standard benchmark redox system-ferrocyanide. The electro of peak-to-peak potential separation, and separation between oxidative and reductive peak potentials
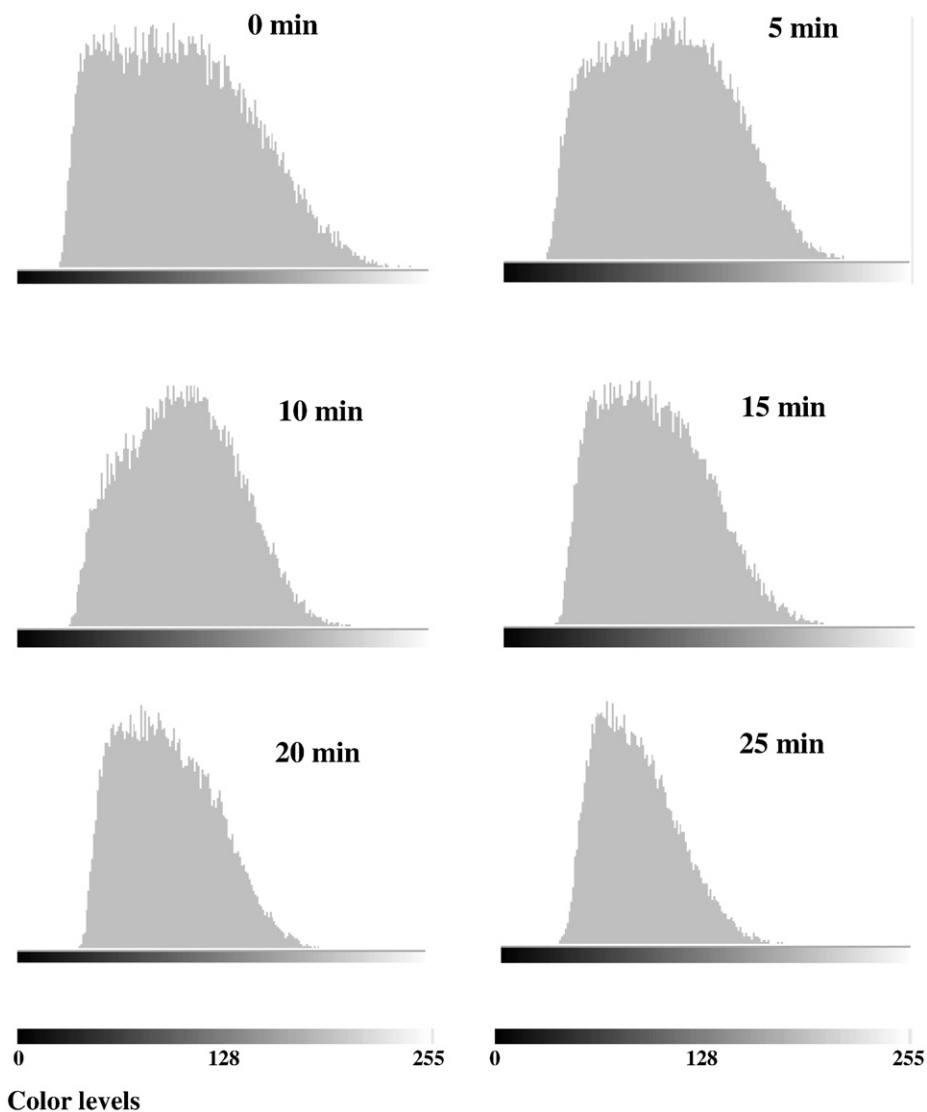
Fig. 3. Schematic representation of the image color level histograms obtained from the SPCE before (0 min) and after exposure to oxygen plasma for 5, 10, 15, 20, and 25 min; color scale was set at 256 gray colors with 0 for black and 255 for white.

of ferrocyanide were studied. The plasma-treated and untreated SPCEs exhibited markedly different cyclic voltammograms for the ferricyanide. The untreated SPCEs only exhibited clear redox peaks to ferricyanide, yielding 440 mV peak-to-peak potential separation at a 50 mV/s scan rate. Interestingly, the peak-to-peak potential

Table 2
Summary of color scale for SPCE before and after the treatment with 100 W oxygen plasma.

Treatment time (min)	Percentage of pixels >170[b] in color level[a] (%)	Percentage of pixels <45[c] in color level[a] (%)
0	7	7
5	5	4
10	2	2
15	2	2
20	1	0
25	1	0

[a] Color scale was set at 256 gray colors (0 for black and 255 for white).
[b] Resin binder was etched from the surface of SPCE due to the oxygen plasma treatment.
[c] Graphite was loosened and removed from the SPCE surface due to the oxygen plasma treatment and formed a flat surface.

separation for ferricyanide on SPCEs was reduced to 156 mV, after oxygen plasma treatment. Indicating the oxygen plasma treatment could enhance the electron transfer rate of SPCEs.

Another batch of SPCEs was subjected to higher plasma powers of 200 W and 300 W. The electrochemical response of the SPCEs increased 150-fold after exposure to 200 W and/or 300 W plasma for 5 min (data not shown). However, these SPCEs had unstable electrochemical responses during repetitive follow-up measurements. The formation of pit-like defects on the graphite surface was the key factor responsible for the increase in electrochemical response. However, the electrochemical response decreased rapidly upon repeated use of the same electrode to detect the same concentration of H_2O_2. This phenomenon was attributed to the erosion of the graphite on the SPCE surface by higher power plasma [37], where a rugged surface is revealed by SEM micrographs (data not shown). Similar results were also reported by another study [22].

4. Conclusions

The inter-electrode, or electrode-to-electrode, reproducibility of conventional carbon paste electrodes is usually poor due to the coverage of graphite powders by pasting binder and other surface
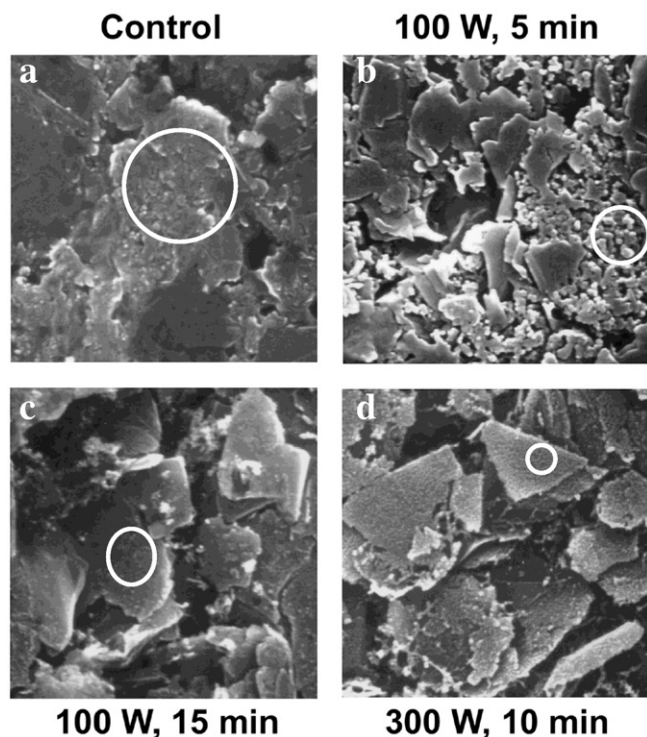
Control

100 W, 5 min

100 W, 15 min

300 W, 10 min

Fig. 4. Scanning electron micrographs of SPCEs with magnification of 7000×. SPCEs were untreated (Fig. 3a, control), treated with 100 W oxygen plasma for 5 min (b), 15 min (c), and treated with 300 W oxygen plasma for 10 min (d) prior to the SEM analysis.

impurities. Typical argon plasma treatment only removes impurities on the SPCE surface and leads to partial release of edge planes that are originally covered with graphite particles. Oxygen plasma treatment of SPCEs at 100 W for 20 min appeared to accomplish optimal removal of the pasting binder from the edge planes and induce pit-like defects in the basal plane of the graphite surface. The reproducibility of SPCEs was improved significantly, with an intra-electrode CV of 4.8% and an inter-electrode CV of 4.6% for the measurement of 1 mM H_2O_2. The inter-electrode reproducibility was significantly affected by the immediate removal of the resin binder by oxygen plasma and heat as soon as it was exposed on the surface of SPCE and was accurately monitored by the color level index presented in this study. When the resin binder of SPCE was chipped off by oxygen plasma, the SPCE surface became relatively smooth, and the effect of oxygen plasma treatment appeared to be correlated with the degree of roughness of the SPCE surface.

This study also examined the quality of electrodes using color level index analysis of the digital black-and-white image data files converted from the optical micrographs of the SPCE surface taken during oxygen plasma treatment. The pixels of the digital image were then categorized in the form of histograms according to their respective color standings in the 256 gray scale, with 0 for black and 255 for white. The statistical histograms of oxygen plasma-treated SPCE were symmetric with relatively narrow-distributions compared to those of untreated SPCEs. The decrease of white level pixels may have been due to the disappearance of resin binder from

the SPCE surface. On the other hand, the decrease in black level was caused by the removal of loosened graphite from the SPCE surface, thereby the contrast of the black and white image decreased. This simple, quick, and inexpensive method may be used to monitor the effect of oxygen plasma treatment on SPCEs. This method has great potential for applications in on-line quality control of the SPCE plasma-treatment process.

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