

# A study on Electrochemical Imaging

Norimasa Iwai\*, Noriyuki Kumazawa\*\*, Manabu Takeuchi\*  
 \* Department of Electrical and Electric Engineering, Ibaraki University,  
 Nakanarusawa, Hitachi, 316-8511 Japan  
 \*\* Faculty of Engineering (Mito Branch), Ibaraki University,  
 Bunkyo, Mito, 310-8512 Japan

## Abstract

An electrochemical imaging method based on methyl orange was proposed and evaluated. A filter paper containing some aqueous solution of methyl orange was placed on an ITO glass electrode, and a platinum wire was used as a counter electrode. A DC voltage was applied between the two electrodes. When the applied voltage was below 1 V, the change in the color near both electrodes was not observed. When the applied voltage was over 2 V, the color of the paper near the anode changed from yellow to red. On the other hand, the color near the cathode did not change from yellow, and the generation of bubble was observed. The change in color near the anode seemed to be originated from the electrolysis of water. The red color formed by applying DC voltage disappeared within several seconds after cessation of applying voltage by the diffusion of the ion in the solution. The retention time of the red color exceeded 60 minutes, when the solution was turned into gel by adding some agar. It was also possible to eliminate the red color near the electrode by changing the polarity of applying voltage.

## Introduction

Recently, researches of new recording technology that replaces paper have been becoming popular and popular. Especially, various researches with the aim of the practical application have been made on rewritable papers. The new imaging technology classified in the rewritable papers has active studies by many workers in the world.

Several systems for the rewritable papers such as twisting ball display [1, 2], microcapsule electrophoresis [3], cards based on leuco-dye [4], etc is proposed at the present. However, these technologies usually need relatively high energy for forming images. For example, the twisting ball display system needs a voltage of more than 1 kV. A high temperature around 100 °C is necessary for the cards using leuco-dye. Other new technologies, which do not need high energies, are desired in the field of rewritable papers.

This study proposes a method for forming images using methyl orange, which is a pH indicator working with a low voltage. The molecular structure of methyl orange and wavelength of its maximum absorbency in red and yellow colors are shown in figure 1. It appears red, when pH of the solution is under 3.1, while, yellow, when pH of

the solution is over 4.4. We tried to apply this color changing system for an electrochemical imaging.

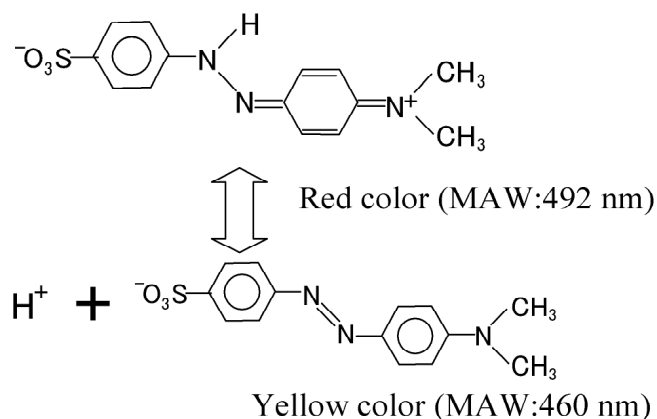


Figure 1. Molecular structure of methyl orange and its maximum absorption wavelengths (MAW) in red and yellow colors.

## Experimental

### Preparation of imaging elements

A piece of filter paper (diameter: 50 mm) was soaked in 0.02% methyl orange water solution. The color of the aqueous solution was yellow, and pH was 6.8. Then, the paper was placed on an ITO glass electrode (area: 250 mm<sup>2</sup>). A platinum wire (Pt) was used as a counter electrode for electrochemical imaging.

### Electrochemical measurements

The relationship between an electric current and applied voltage was measured on the paper containing methyl orange solution. A DC voltage was applied between two electrodes (Pt and ITO) as shown in figure 2. A platinum plate (area: 10 mm × 10 mm) was used instead of the platinum wire in only this measurement. A function generator (Wavetek, Model 19) was used for applying DC voltage to the paper. The electric current was monitored with an electrometer (Advantest, TR8652). The platinum

generator (Wavetek, Model 19) was used for applying DC voltage to the paper. The electric current was monitored with an electrometer (Advantest, TR8652). The platinum works as an anode in this study and color change in the paper occurs by the anode. The applied voltage was changed from 0V to 10V. Change in color was examined as a function of applied voltage.

#### Measurements of absorbency

The color formed in filter paper usually disappeared in several decades of seconds after cessation of applying voltage. In order to extend the retention time of color in the paper, some agar was added into methyl orange aqueous solution. The agar turned the methyl orange solution into gel, and extended the retention time of color in the paper longer than 1 hour. As a result, qualitative characterization of color change in the paper could be available. For that purpose, an UV-visible spectrophotometer (Shimadzu, UV1200) was used, and change in the absorption spectrum of the gel with time was monitored. The absorption spectra were measured in the wavelength region of from 350 to 600 nm.

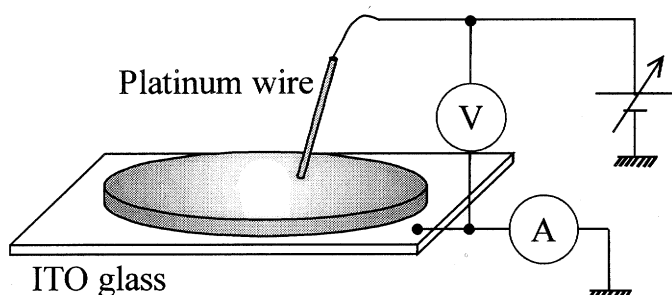


Figure 2. Experimental set up for electrochemical imaging used in this study

## Results and Discussion

Figure 3 shows the relationship between electric current density and applied DC voltage for the paper containing methyl orange aqueous solution. The voltage on the abscissa was applied to the platinum electrode.

The electric current density increased rapidly over applied voltage of 2.5V. When the applied voltage was larger than 2.5V, generation of bubble was observed around both the electrodes. The color near the anode changed from yellow to red associated with the generation of bubble. On the other hand, the color near the cathode did not change from yellow.

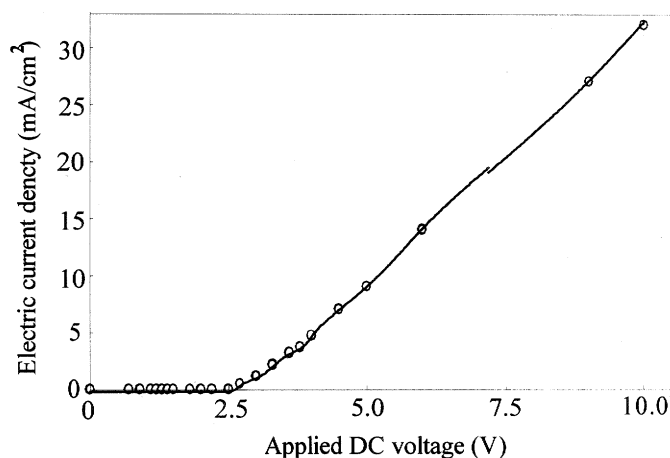
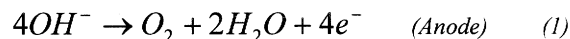


Figure 3. Relationship between electric current density and applied DC voltage for the paper containing methyl orange aqueous solution.

It is well known that water is electrolyzed when a voltage over the voltage of electrolysis is applied and bubble is generated near the both electrodes. The reactions, which proceed at anode and cathode, are represented by the following equations.



Since hydroxide ions are consumed at the anode, pH decreases around that electrode. Therefore, the color of methyl orange changes to red when pH is lower than 3.1. While the pH around the cathode increases. However, the color change around the cathode could not be observed. Methyl orange shows yellow color in the region over pH 4.4. Therefore, the change in color does not occur in this experiment, even if pH near the cathode increases over 6.8. Imaging of red characters on the yellow paper was performed by applying voltage of over 2.5V to the anode made of a platinum wire. An image sample prepared by this system is given in figure 4.



Figure 4. An imaging sample formed by applying DC voltage of 9V.

As described before, however, those red characters disappeared within several decades of seconds by the diffusion of the ions. Then, the solution was turned into gel by adding agar in order to reduce diffusion rate of the ions.

The absorption spectrum was measured for quantitatively evaluation of the color change of the gel. First, absorption spectrum of the gel (yellow) was measured at the applied voltage 0V. Next, a voltage was applied until the color of the gel changed to red and the absorption spectrum of the gel (red) was measured. The maximum absorption wavelengths were found to be 492 nm and 460 nm in red and yellow states, respectively. The absorbency of the gel in red was higher than the yellow gel. This is because the molar extinction coefficient of red gel is higher than yellow gel.

The absorption spectrum of the gel changed with elapsed time after the color change to red as shown in figure 5. Absorbencies around 492 nm and 460 nm decreased and increased with an increase in elapsed time, respectively. As a result, the color of the gel returned to the original color, yellow, after several decades of minutes.

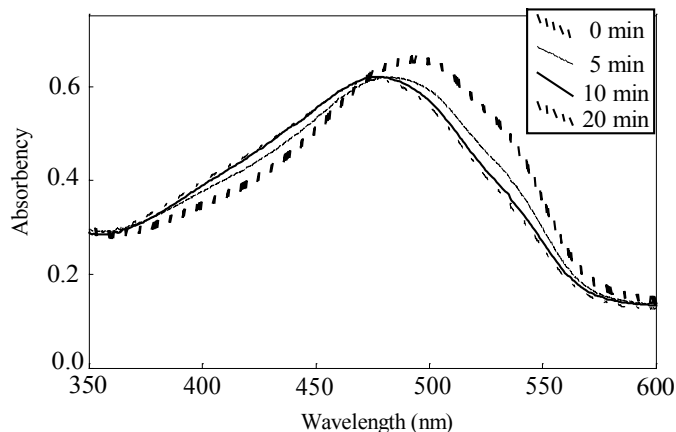


Figure 5. Change in absorption spectrum of the gel with elapsed time after cessation of applying DC voltage.

The absorbencies at 492 nm and 460 nm as a function of elapsed time are shown in figure 6. It can be confirmed that the absorbency at 492nm decreased gradually, while the absorbency at 460nm increased reversibly. Both the absorbencies at 492nm and 460 nm did not change beyond about 13 minutes, and further color change did not occur.

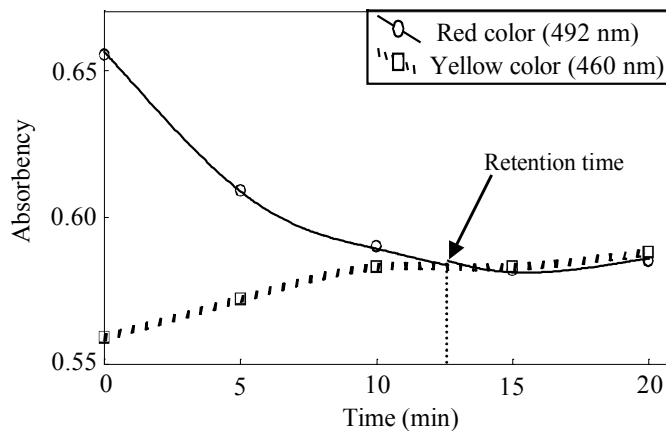


Figure 6. Evaluation of the retention time of color.

The retention time of color is defined by the intersection of the two absorbency curves at 492nm and 460nm in this paper. The color retention time of the gel was about 13 minutes at the agar concentration of 2 wt%. When the concentration of agar added to the methyl orange solution increased to 10 wt%, the color retention time increased to over 60 minutes.

The image contrast is defined by the following equation.

$$\text{Contrast} = (I_{492} - I_{460}) / (I_{492} + I_{460}) \quad (3)$$

Where,  $I_{492}$  and  $I_{460}$  represent absorbencies at 492nm and 460nm, respectively. A contrast of 0.19 was obtained in this study, which was low but could be recognized.

Finally elimination of the red color near the electrode was confirmed by changing the polarity of applying voltage. Details of this phenomenon are now under further studying.

## Conclusion

An electrochemical imaging system based on methyl orange was proposed and evaluated and following results were obtained.

1. The color of filter paper containing methyl orange solution was changed from yellow to red by applying a DC voltage to the paper with a platinum electrode.

2. The dispersion rate of the ion could be lowered by turning methyl orange aqueous solution into gel, and a color retention time over 60 minutes was achieved.
3. The image contrast between red and yellow was 0.19.

## References

- [1] N. K. Sheridan, *Pan-Pacific Imaging Conference /Japan Hardcopy '98*, pg. 83 (1998).
- [2] T. Tanikawa, M. Omodani, Y. Takahashi, *Proc. Japan Hardcopy 2000*, pg. 65 (2000) [in Japanses].
- [3] H. Kawai, N. Kanae, *Proc. Japan Hardcopy '99*, pg. 237 (1999) [in Japanses].
- [4] M. Torii, H. Furuya, T. Tatewaki, K. Tsutsui, *Proc. Japan Hardcopy '99*, pg. 213 (1999) [in Japanses].

## Biography

Norimasa Iwai received his B. Eng. in Electrical and Electronic Engineering from Ibaraki University in 1999. He is now working for M. Eng. at the same university. He is studying charging characteristics of toners, application of electret to the developing process in electrophotography and electrochemical imaging.