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Use of RGB digital video analysis to study electrochemical processes involving color changes

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ABSTRACT

Color changes on an electrode surface during the course of electrochemical processes were monitored by in situ digital video recording. The evolution of standard red, green and blue (sRGB) intensity channels extracted from digital images showed a close relationship with the electrochemical processes taking place. In particular, the derivative of the sRGB mean intensity with respect to time ($d\overline{I}/dt$) gave useful insights into the electrochemical mechanism. The standard deviation (*std*) of the sRGB intensity provided information about the color homogeneity of the studied region on the electrode surface. We selected poly(*o*-toluidine) electrochromism on a transparent electrode and anodic copper dissolution on an opaque electrode as examples. Independently of electrode transparency and area, we were able to separate electrochromic processes, to monitor fast electrochromic changes and to evaluate the spatial distribution of metal dissolution on a composite electrode. These results show great promise for use in innovative investigations and for fast, low-cost quality control of electrochromic devices or modified electrodes.

1. Introduction

Electrochromic materials (EMs) generate tunable colors in response to electrical stimulation [1], and are often studied using spectroelectrochemistry, a technique which combines the information obtained by reaction-oriented electrochemistry and species-focused visible spectroscopy [2]. Applications include identification of redox sites and intermediates, deconvolution of multistep redox reactions, contrast or transmittance characterization and monitoring of electrochemical-induced film degradation [3–6].

The optical properties of EMs are usually investigated using relatively small electrode areas and transparent electrodes. However, in view of the fact that the uniform deposition of EMs depends on the electrode geometry [7], among other things, the characterization of the large areas necessary in quality control of finished devices is tedious as control spectra are required to be taken at strategic points using classical spectroscopy. Furthermore, only opaque electrodes with a smooth surface can adequately reflect the radiation to be analyzed by reflectance spectroscopy since rough electrodes decrease and scatter the reflected spectroscopic signal.

Digital image acquisition is a non-contact, non-invasive, and cost-effective technology which could overcome these problems since it allows characterization of opaque and/or large colored electrode areas and their evolution during the electrochemical process. This technique has been used, for example, in assessing the quality of fruits [8], in colorimetric sensors [9] and in solar cells [10]. However, the analysis of primary colors (standard red, green, blue or sRGB) from digital images has not been widely used to investigate electrochemical systems due to the extensive use of conventional spectroscopy. Pitting in metal surfaces [11], optical sensors [12] and the enhancing of latent fingerprints [13] are some areas in which sRGB digital image analysis (sRGB-DIA) from single or sequential digital pictures have been of proven utility in the electrochemical field. However, studies of the kinetics of many electrochemical processes require fast image acquisition.

The motivation of this work was to demonstrate that sRGB-DIA of images acquired by digital video at short time intervals (up to 25 frames/s) can be very useful in studying electrochemical processes involving color changes on the electrode surface. Interestingly, the derivative of the sRGB mean intensity with respect to time ($d\overline{I}/dt$) revealed hidden aspects of the reaction mechanism, while the standard deviation (*std*) of the sRGB intensity provided information about the color homogeneity of the studied surface. The examples investigated were the electrochromic behaviour of poly(*o*-toluidine) (POT) on transparent indium-tin oxide (ITO) electrodes and copper dissolution on black composite electrodes.

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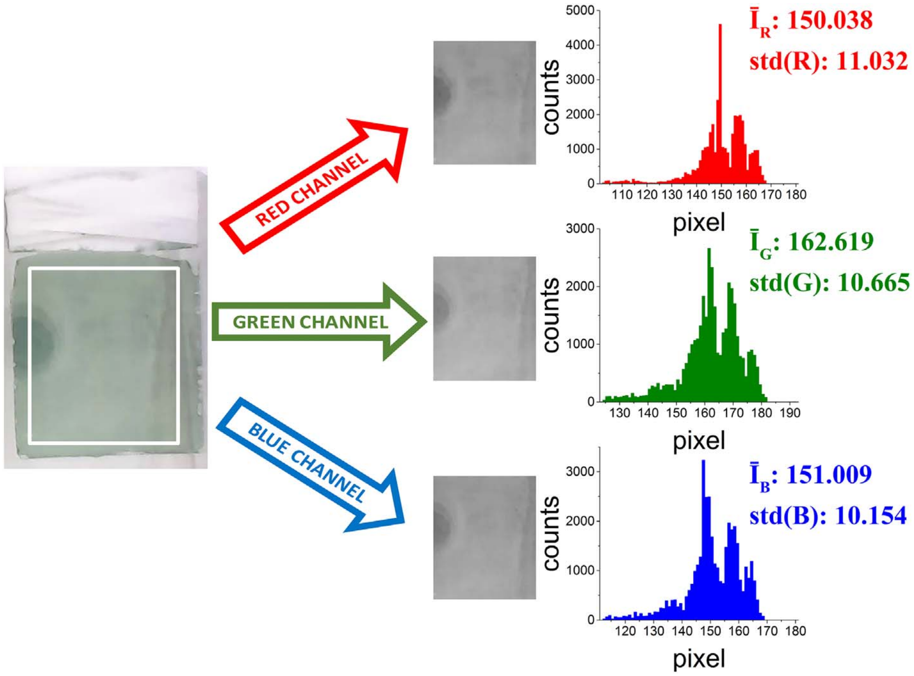

Fig. 1. Schematic diagram of the sRGB-DIA process. From left to right: selection of the region under study (white square), decomposition into sRGB channels, histogram representation, mathematical calculation of $\overline{I_i}$ and *std*(*i*).

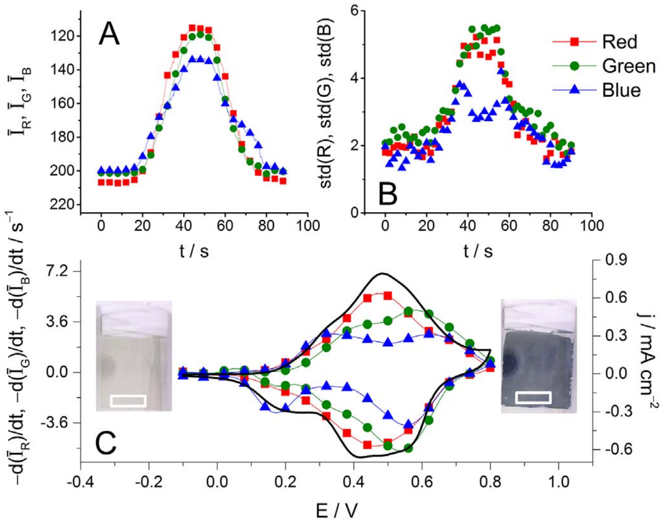

Fig. 2. sRGB-DIA during cyclic voltammetry of POT in 0.5 M H_2SO_4: (A) $\overline{I_i}$; (B) *std*(*i*); and (C) d($\overline{I_i}$)/d*t* and voltammogram.

2. Experimental

2.1. Apparatus

The electrochemical experiments were performed using a PAR 273A potentiostat/galvanostat. ITO (30 Ω cm^2) or a composite composed of graphite and copper powder randomly dispersed into a polypropylene matrix (CCuPP, 40:10:50 by weight) were used as working electrodes; a platinum mesh was the counter electrode and Ag|AgCl|$KCl_{(sat)}$ was the reference electrode. The electrochemical cell was a 2 × 2 cm high-transmittance glass cell (Hellma, OG quality). A digital endoscope camera (EPA-503278) with a USB connection was used to capture 640 × 480 color digital videos at a rate of up to 25 frames/s. The digital images obtained from the video were sRGB jpg files, with 8 bits per channel. The electrochemical cell was illuminated in a home-made white box with a T5 6400K fluorescent tri-phosphor lamp (color rendering index 80).

2.2. Electrode modifications

POT was deposited on the ITO substrate by applying 1 mA for 100 s in 0.5 M H_2SO_4 (Fisher scientific) and 0.2 M *o*-toluidine (Fluka). The electrochemical response of POT in 0.5 M H_2SO_4 was obtained by cyclic voltammetry between −0.2 V and 0.8 V at 20 mV s^{-1}. The color transformation of POT in 0.5 M H_2SO_4 was performed by chronoamperometry, applying −0.1 V for 10 s and then 0.8 V for 2900 s. Copper was deposited by chronopotentiometry on CCuPP by applying −8 mA for 1800 s in 0.5 M $CuSO_4$ (Scharlau) and 0.1 M H_2SO_4 and was dissolved in 0.1 M H_2SO_4 by applying 8 mA for 2000 s. All reagents were analytical grade, used as received and dissolved in Milli-Q-plus H_2O (resistivity 18.2 MΩ cm).

2.3. Image processing

Digital full-color videos synchronized with the electrochemical experiments were separated at suitable regular intervals (min. 0.04 s) into a series of images in jpg format. We automatically read the image files and selected the region under study (white rectangles on electrode images) using Mathcad® v14 software. The cropped images were decomposed into sRGB intensity arrays. The intensities may vary from 0 to 255 to create the corresponding gray-scale images (Fig. 1). Color histograms showed the statistical distribution of array intensities characterized by two statistical parameters: the mean ($\overline{I_i}$) and standard deviation of intensity (*std*(*i*)) for each color channel ($i = R, G, B$). If $\overline{I_i}$ tends to 0, this indicates an increase in the color intensity, if not, $\overline{I_i}$ tends to 255 as the color intensity decreases. Lower *std*(*i*) values indicate that array intensities tend to be close to $\overline{I_i}$. Thus, *std*(*i*) reveals the color distribution in the analyzed region, with a relative low *std*(*i*) corresponding to a more homogeneous colored surface than a higher *std* (*i*).