Lab Report 2


***Abstract***

In Lab Report 1, we described the fabrication and testing of two dynamic windows that both consisted of a fluorine tin oxide (FTO) working electrode. However, the underlying mechanism that contributed to the differences in performance of the two windows was still unclear. In this study, we used a scanning electron microscope (SEM) to characterize the surface morphology of the working electrodes of both dynamic windows and employed X-Ray photoelectron spectroscopy (XPS) to characterize the presence and chemical state of metals on the surfaces of both dynamic windows. We hypothesized that the functional window (Window 1) and the broken window (Window 2) had differences in their surface morphology. In this study, we found that Window 1 in the dark state had more dense, platelet-like particles uniformly covering the surface of the working electrode than Window 2 did in the dark state. We also found that the surface morphology of Window 1 was more spherical than the one of Window 2. Additionally, we found that the Bi/Cu ratio of Window 1 was 1.0:11.0 and the Bi/Cu ratio of Window 2 was 1.5:1.0.


***Introduction***

In Lab Report 1, we described the fabrication and testing of two dynamic windows that both consisted of fluorine tin oxide (FTO) working electrodes and utilized the reversible electrodeposition of Copper-Bismuth (Cu-Bi). We found that one of the windows (Window 2) was broken due to an open circuit while another one was functional (Window 1). We also reported that we first cycled Window 1 for 5.5 times and found that it exhibited reversible cycling between the clear state with an average transmittance of 55% and the dark state with an average transmittance of 5%. We then cycled Window 1 for 10 more times and found it exhibited reversible cycling between the clear state with an average transmittance of 30% and the dark state with an average transmittance of 10%.

Based on our results in Lab Report 1, we hypothesized that the broken window (Window2) and the functional window (Window 1) had differences in their surface morphology.

In Lab 6 and 7 we set out to characterize the morphology and elemental composition of Window 1 and Window 2 to understand the mechanism of the discrepancy in their performance. More specifically, in Lab 6, we used a scanning electron microscope (SEM) to characterize the surface morphology of the working electrodes of both dynamic windows in the dark state. In Lab 7, we employed X-Ray photoelectron spectroscopy (XPS) to characterize the presence and chemical state of metals on the surfaces of both dynamic windows.

## ***Experimental Design***

### ***Lab 6***

### **SEM Lab**

The setup of the Lab 6 experiment involved the following instrument: Apreo S LoVac Scanning Electron Microscope from Thermo Fisher Scientific. The acceleration voltage of the electron beam used for image acquisition was 5.00 kV.

### ***Lab 7***

### **XPS Lab**

The setup of the Lab 7 experiment involved the following instrument: Physical Electronics, Inc. (PHI) VersaProbe 3 from Physical Electronics, Inc.

The source of the X-ray was Aluminum K Alpha (Al Kα) and the energy of the X-ray was 1.4866 keV (1486.6 eV).

## ***Results and Discussion***

### ***Lab 6***

### **Morphology Images**

It is important to notice that Window 2 did not work during Lab 4 but worked after two weeks when we attempted to cycle both Window 1 and Window 2 to their dark states in Lab 6.

For each of the windows, we used the SEM to obtain a low (6500 x) and a high (80000 x) magnification image representative of the morphology of the windows in the dark state.

Based on Figure 1a and Figure 1c as shown below, we found that the main difference between the low magnification image representatives of the morphology of the two windows in the dark state was that Window 1 had more dense, platelet-like particles uniformly covering the surface of the working electrode than Window 2 did. There were more and larger dark areas in Window 2 than in Window 1. This means more surface areas of Window 2 were not covered by the metal particles. Based on Figure 1b and Figure 1d shown below, we found that the main difference between the high magnification image representatives of the morphology of the two windows in the dark state was that there were more dendritic structures in Window 2 than in Window 1. By comparing Figure 1b and Figure 1d, we found that the surface morphology of Window 1 was more spherical than the one of Window 2.

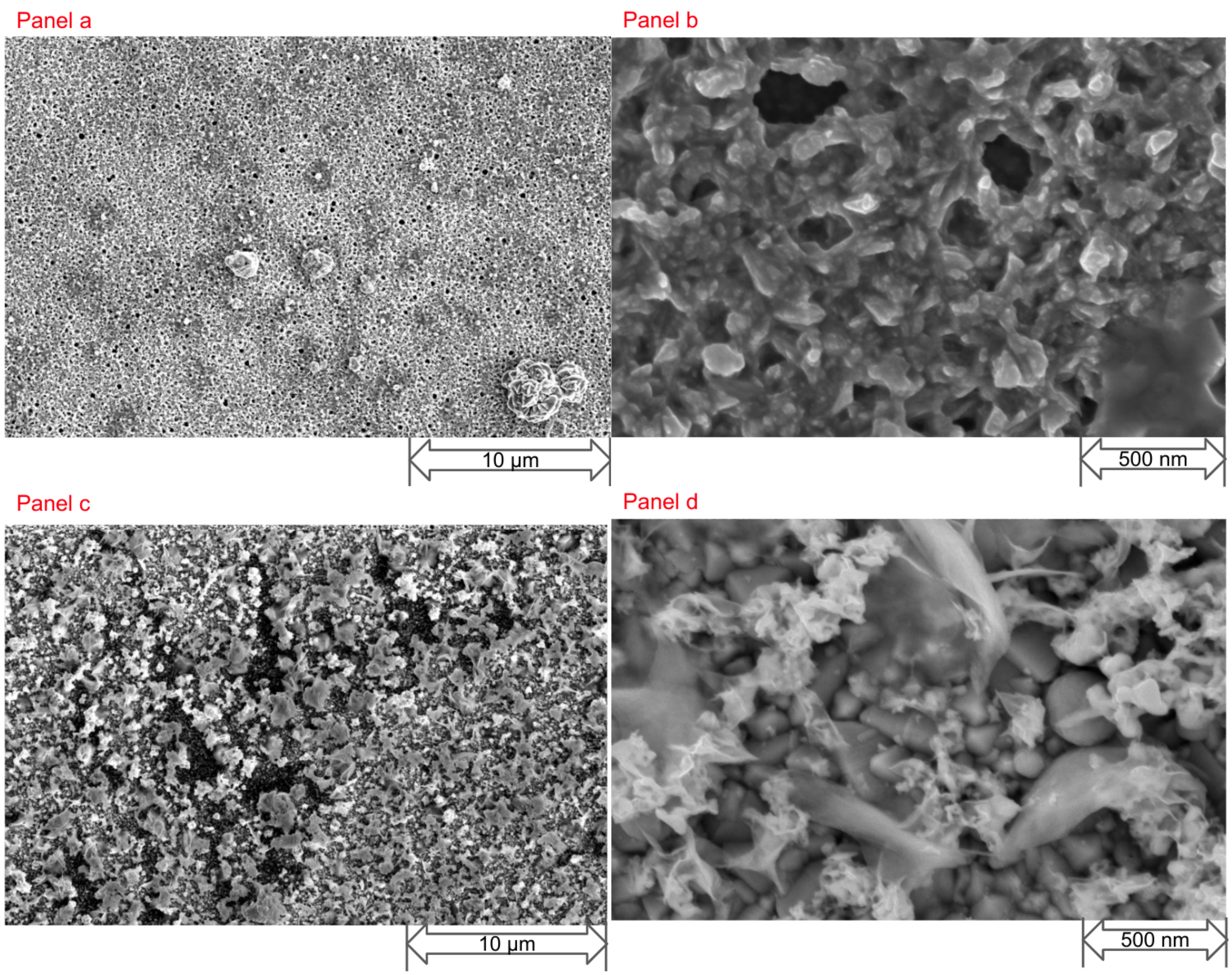



Figure 1: SEM images for Window 1 and Window 2 with different magnifications. Panel a: The image representative of the morphology of Window 1 in the dark state with 6500 x magnification. Panel b: The image representative of the morphology of Window 1 in the dark state with 80000 x magnification. Panel c: The image representative of the morphology of Window 2 in the dark state with 6500 x magnification. Panel d: The image representative of the morphology of Window 2 in the dark state with 80000 x magnification.

Based on the panels shown above in Figure 1, to correlate the morphological differences between the samples with their strip chart results from Lab Report 1, we first recall that Window 1 had consistent strip chart results while Window 2 did not have any strip chart results. The presence of the consistent strip chart results for Window 1 indicates the reliability of Window 1 in recycling. On the other hand, the lack of strip chart results for Window 2 was a good indicator of the lack of recyclability of Window 2.

According to McGehee et al. [1], the presence of dendrites is usually a good indicator of the lack of recyclability in the dynamic windows. As a result, the dendritic morphology of metal deposits with poor coverage of the surface of the working electrode as shown in Figure 1c and Figure 1d, which represented a low coverage of Bi-Cu on the working electrode of Window 2, likely led to the lack of recyclability in Window 2 and the lack of strip chart results for Window 2.

Moreover, according to McGehee et al. [1], uniform coverage of Bi-Cu usually gives the working electrode the ability to receive and lose electrons uniformly. If there are more dendrites on the working electrode of a dynamic window, then the window cannot leverage the entire electrode to facilitate the electrodeposition. As a result, the reversibility of the window would be limited. This could explain why Window 1 had consistent strip chart results and Window 1 had better recyclability than Window 2. Therefore, we could reason that a working electrode with a more dense and more uniform platelet-like particle coverage as well as with a more spherical surface morphology positively correlated with better recyclability of a dynamic window.

***Lab 7***

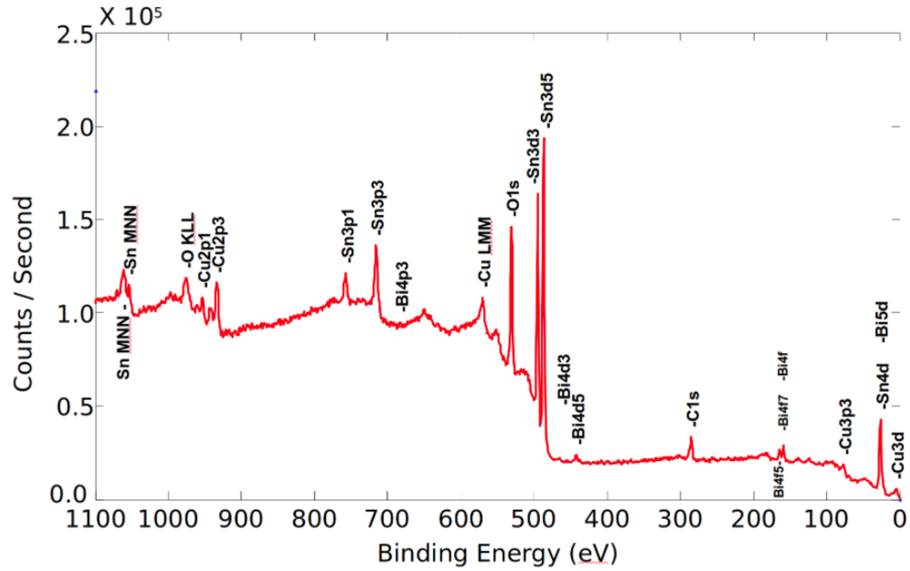
**XPS Spectra**

Based on Figure 2a as shown below, we had the peak assignments of the key elements – including bismuth (Bi), copper (Cu), indium (In), and tin (Sn) – for Window 1 XPS spectrum.

Window 1 had Sn with the following binding energies: 1060 eV, 1055 eV, 760 eV, 725 eV, 495 eV, 480 eV, and 40 eV. Window 1 had Cu with the following binding energies: 950 eV, 930 eV, 570 eV, 80 eV, and 5 eV. Window 1 had Bi with the following binding energies: 680 eV, 450 eV, 430 eV, 165 eV, 160 eV, and 40 eV. Window 1 had no In based on the Window 1 XPS spectrum.

Based on Figure 2b as shown below, we had the peak assignments of the key elements – including Bi, Cu, In, and Sn – for Window 2 XPS spectrum. Window 2 had Sn with the following binding energies: 760 eV, 710 eV, 495 eV, 490 eV, and 25 eV. Window 2 had Cu with the following binding energies: 950 eV, 930 eV, 570 eV, and 5 eV. Window 2 had Bi with the following binding energies: 680 eV, 460 eV, 440 eV, 165 eV, 160 eV, and 25 eV. Window 2 had no In based on the Window 2 XPS spectrum.

Panel a




Panel b

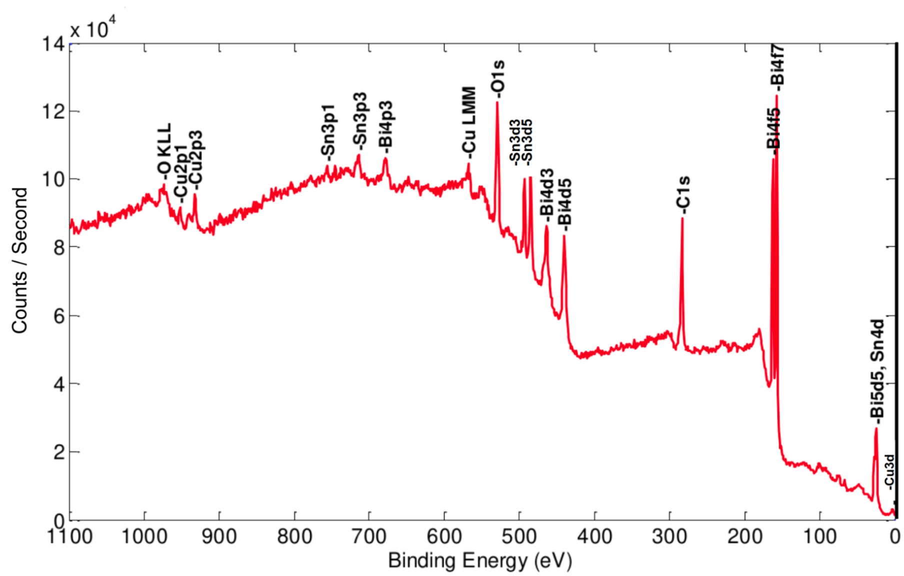


Figure 2: Full range XPS survey spectrum of the windows in the dark state. Panel a: XPS survey spectrum with peak assignments of Window 1. Panel b: XPS survey spectrum with peak assignments of Window 2.

Based on Figure 2 as shown above, both Window 1 and Window 2 had oxygen (O) and carbon (C) with the same binding energies. In addition, both Window 1 and Window 2 did not have indium.

The main differences between the two samples we had with the XPS were that Window 1 had Sn MNN with binding energies of 1060 eV and 1055 eV, whereas Window 2 did not have Sn MNN with binding energy in the range between 1000 eV and 1100 eV. Window 1 also had Bi4f with a binding energy of 160 eV, whereas Window 2 did not have Bi4f with binding energy in the range between 100 eV and 200 eV. Moreover, Window 1 had Cu3p3 with a binding energy of 80 eV, whereas Window 2 did not have Cu3p3 with binding energy in the range between 0 eV and 100 eV. Moreover, the Bi/Cu ratio of each of the two Windows was also different. Based on our calculation, we found that the Bi/Cu ratio of Window 1 was 1.0:11.0 and the Bi/Cu ratio of Window 2 was 1.5:1.0.

To correlate the Bi/Cu ratio differences between the samples with the SEM images in Lab 6 as shown in Figure 1, recalled that Window 1 had a more spherical surface morphology and more uniform metal deposits than those of Window 2 based on Figure 1. McGehee et al. [1] report that increasing the concentration of copper usually leads to a more uniform coverage of metal deposits and a more spherical surface morphology with fewer formations of dendrites. In our case, a lower Bi/Cu ratio would correspond to a higher concentration of copper in the window. Recall that we found that the Bi/Cu ratio of Window 1 was 1.0:11.0 and the Bi/Cu ratio of Window 2 was 1.5:1.0. This meant there was a higher copper concentration in Window 1 than in Window 2. As a result, we could reason that an increase in the concentration of copper positively correlated with a more uniform coverage of metal deposits and a more spherical surface morphology. The correlation we obtained from Lab 6 and Lab 7 was consistent with the results reported by McGehee et al. [1].

To correlate the Bi/Cu ratio differences between the samples with the strip chart results in Lab 4 from Lab Report 1, we first recall that Window 1 had consistent strip chart results while Window 2 did not have any strip chart results. The presence of the consistent strip chart results for Window 1 indicates its reliability in recycling. On the other hand, the lack of strip chart results for Window 2 was a good indicator of the lack of recyclability of Window 2. Recall that, based on Figure 1a and Figure 1c, we found that Window 1 had more platelet-like particles uniformly covering the surface of the working electrode than Window 2 did. And recall that there was a higher copper concentration in Window 1 than in Window 2. Therefore, we could reason that an increase in the concentration of copper positively correlated with better recyclability of a dynamic window.

Overall, the results from Lab 6 and Lab 7 supported our hypothesis that Window 1 and Window 2 had differences in their surface morphology.

## ***Conclusion***

In this study, we found that Window 1 in the dark state had more dense, platelet-like particles uniformly covering the surface of the working electrode than Window 2 did in the dark state. In addition, we found that the surface morphology of Window 1 was more spherical than the one of Window 2. Finally, we found that the Bi/Cu ratio of Window 1 was 1.0:11.0 and the Bi/Cu ratio of Window 2 was 1.5:1.0.

Our hypothesis was proven since there were observable differences in the SEM images and there was a difference between the Bi/Cu ratio of Window 1 and the Bi/Cu ratio of Window 2.

## ***Reference***

[1] Hernandez, T. S., Barile, C. J., Strand, M. T., Dayrit, T. E., Slotcavage, D. J., & McGehee, M. D. (2017). Bistable black electrochromic windows based on the reversible metal electrodeposition of Bi and Cu. *ACS Energy Letters*, *3*(1), 104-111.