



1.1 Electrochemical System

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In general, the electrochemical system composed of anode and cathode. It divided into two electrode system and three electrode system.

1.1.1 Two electrode system

In two electrode system, which includes working electrode (WE) and counter/reference electrode (CE/RE) to measure the potential across the complete cell. (see Figure 1) It can be used to determine i-E curve in polarographic experiment, energy storage like as battery, fuel cell etc., and electrochemical impedance measurement.

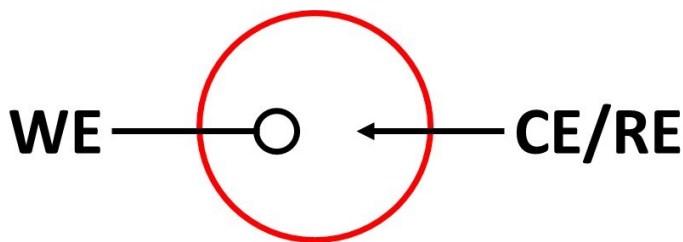


Figure 1 Two electrode system

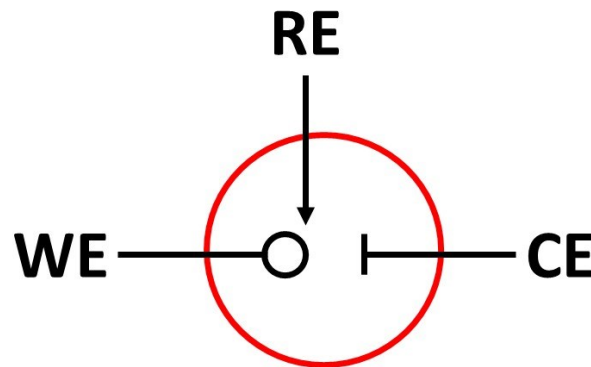


Figure 2 Three electrode system

References

- (1) Allen J. Bard, Larry R. Faulkner, *Electrochemical Methods and Applications* 2nd, 2001
- (2) Joseph Wang, *Analytical Electrochemistry* 2nd ed., 2000

1.1.2 Three electrode system

The most common electrochemical system, three electrode system, composed of working electrode (WE), counter electrode (CE) and a separated reference electrode (RE) to measure the potential and current precisely. (see Figure 2)

Working electrode works as an electron donor or acceptor to the analyte with the suitable potential in the electrolyte. It is preferred to use the working electrode with high signal to noise response and wide potential window for electroanalysis. Several materials such as carbon, mercury, platinum and gold are widely employed in the field of electrochemistry. The potential window of carbon, platinum and gold are charted as shown in Figure 3. (0.1M PBS, pH7 (vs. Ag/AgCl))

And the counter electrode plays the opposite role to the working electrode, it should not participate with the electrochemical reaction except to balance the current observed at the working electrode. The common use of counter electrode is platinum with the characteristic of high stability and conductivity to accomplish the current path. And the reason why the surface area of counter electrode is well advised 10 times larger than the surface area of working electrode is hopefully to catch as much electrons as possible through counter electrode.

References

- (1) Allen J. Bard, Larry R. Faulkner, *Electrochemical Methods and Applications* 2nd, 2001
- (2) Joseph Wang, *Analytical Electrochemistry* 2nd ed., 2000

1.1.3 Potential window

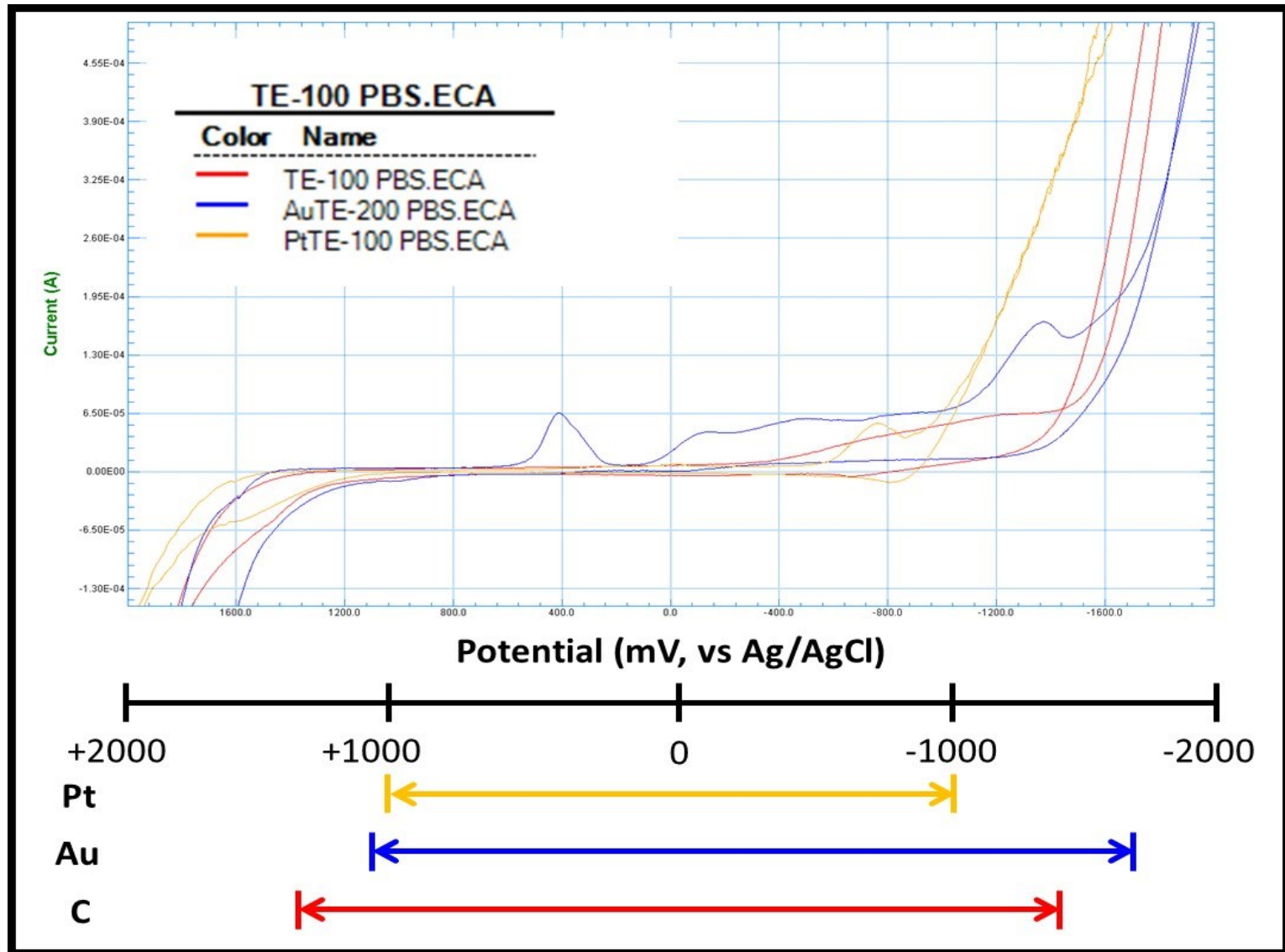


Figure 3 Potential Window

1.1.4 Potential drop

The typical reference electrode should be an ideal non polarizable electrode which is no current flowed through. And it is preferred to be constantly placed as close as a distance of $2d$ to the working electrode (d : tip diameter of reference capillary) to avoid shielding problem or to minimize the potential drop caused by the cell resistance between WE and CE (iR_{cell}). But still, it is difficult to remove the resistance between WE and RE, which is called uncompensated resistance (iR_u). (see Figure 4)

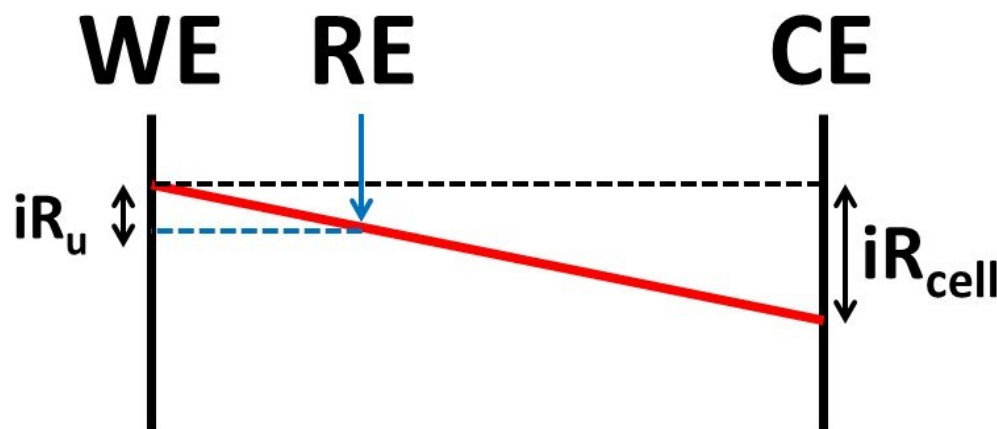


Figure 4 Potential drop

References

- (1) Allen J. Bard, Larry R. Faulkner, *Electrochemical Methods and Applications* 2nd, 2001
- (2) Joseph Wang, *Analytical Electrochemistry* 2nd ed., 2000

1.1.5 Reference electrode

There are many types of reference electrodes employed in the electrochemical system. The most common reference electrodes and its relative potential which respected to the Normal Hydrogen Electrode are charted as shown in Figure 5. In addition, the concentration of potassium chloride in traditional silver / silver chloride reference electrode must be constant to avoid the reference potential shifting. And there is nothing to worry about the potential shift in screen printed three electrode system.

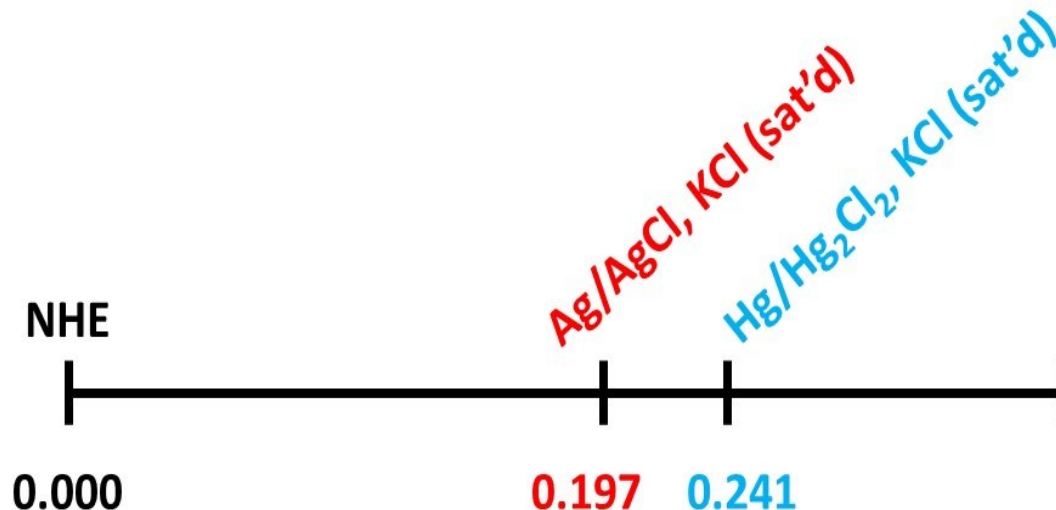


Figure 5 Potential of reference electrodes at 25°C

References

- (1) Allen J. Bard, Larry R. Faulkner, *Electrochemical Methods and Applications* 2nd, 2001
- (2) Joseph Wang, *Analytical Electrochemistry* 2nd ed., 2000

1.1.6 Screen printed three electrode system

The advantage of using the screen printed three electrode system is extremely easy to make an ideal ratio of area of WE/CE and the perfect distance between WE and RE. (see Figure 6)

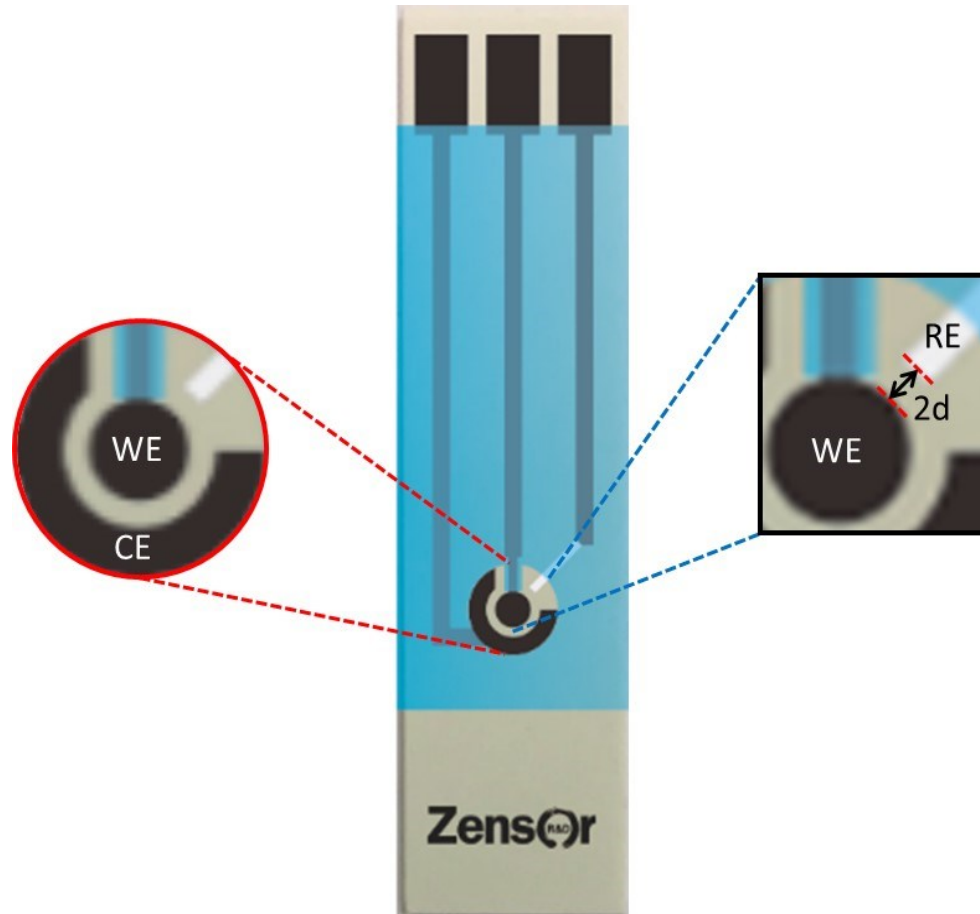


Figure 6 Screen printed three electrode system

1.1.7 Mass transfer

Mass transfer is a big role in the electrochemical process in which brings the electroactive analyte to the surface of working electrode with three different ways. (Diffusion, Migration and Convection)

Diffusion, naturally happened under a concentration gradient, that is the movement of analyte from area of high concentration to the area of low concentration which is in order to minimize the difference of concentration.

Migration is also a natural phenomenon that the charged analyte moves forward to the working electrode (attractive) or goes away (repulsive) under the electric field.

Convection, there are two kinds of convection which are natural and forced. Natural convection is caused by the density gradient. And forced convection occurs with man-made flowing of solution (such as stirring or rotation) to make the analyte moving forward to the surface of working electrode and then undergoes the electron transfer.

References

- (1) Allen J. Bard, Larry R. Faulkner, *Electrochemical Methods and Applications* 2nd, 2001
- (2) Joseph Wang, *Analytical Electrochemistry* 2nd ed., 2000