



## 1.2 Electrochemical Methods

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There are more than 30 methods can be employed in electrochemistry. In this chapter, we will discuss the fundamental methods of the Cyclic Voltammetry (CV), Linear Sweep Voltammetry (LSV), Square wave Voltammetry (SWV), Differential Pulse Voltammetry (DPV), Amperometry (IT), and Open Circuit Potential-Time (OCP).

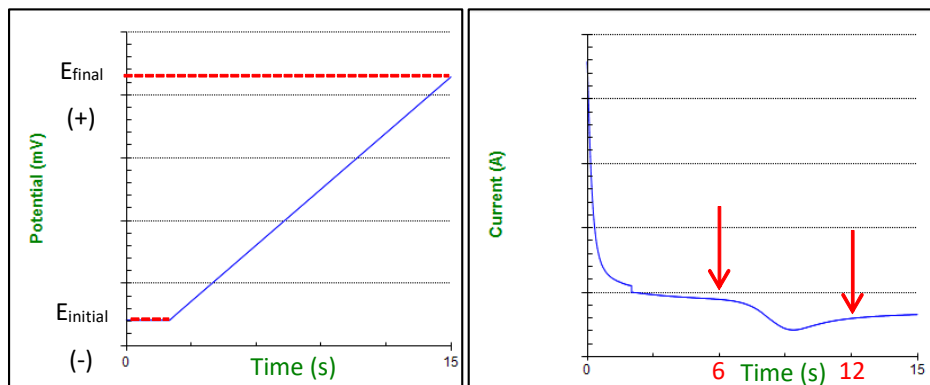
## 1.2.1 Linear Sweep Voltammetry and Cyclic Voltammetry

Voltammetry is one of most widely employed electrochemical method in the world. Basically, it is used to get electrochemical information of analyte by measuring the current of analyte as the function of potential and time. Its waveform goes with continuously or steps like a ladder. In continuous waveform, it divided into linear sweep a segment and cyclic scanning which named LSV and CV. (see Figure 1(a) and Figure 3(a))

For example, 30 mM of ferricyanide was oxidized at a screen printed carbon electrode with the method of LSV as shown in Figure 1 and 2, the potential started at  $E_{\text{initial}}$  and ended at  $E_{\text{final}}$  with a continuous waveform (see Figure 1 (a)), and the resulted current versus time is illustrated as shown in Figure 1(b). It is clearly that the oxidized current with applied potential was started obtaining at the time of 6th second and getting steady state after 12th second.

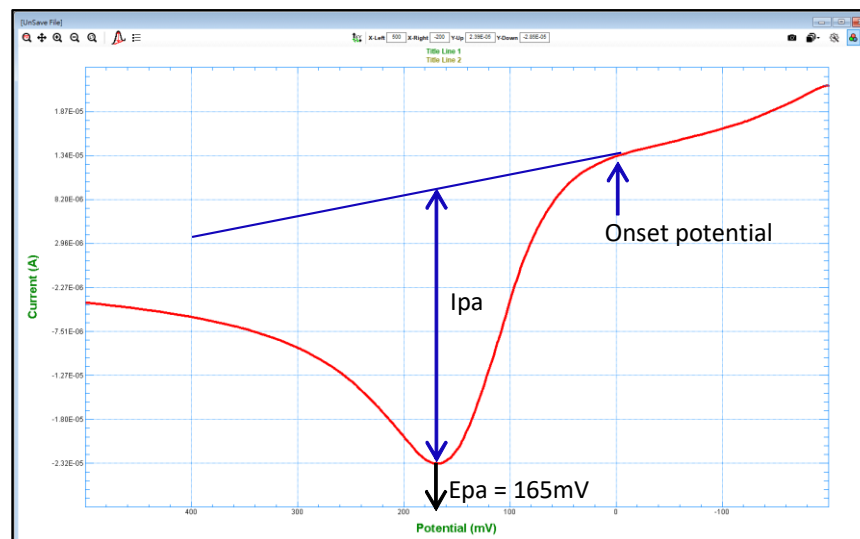
### References

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



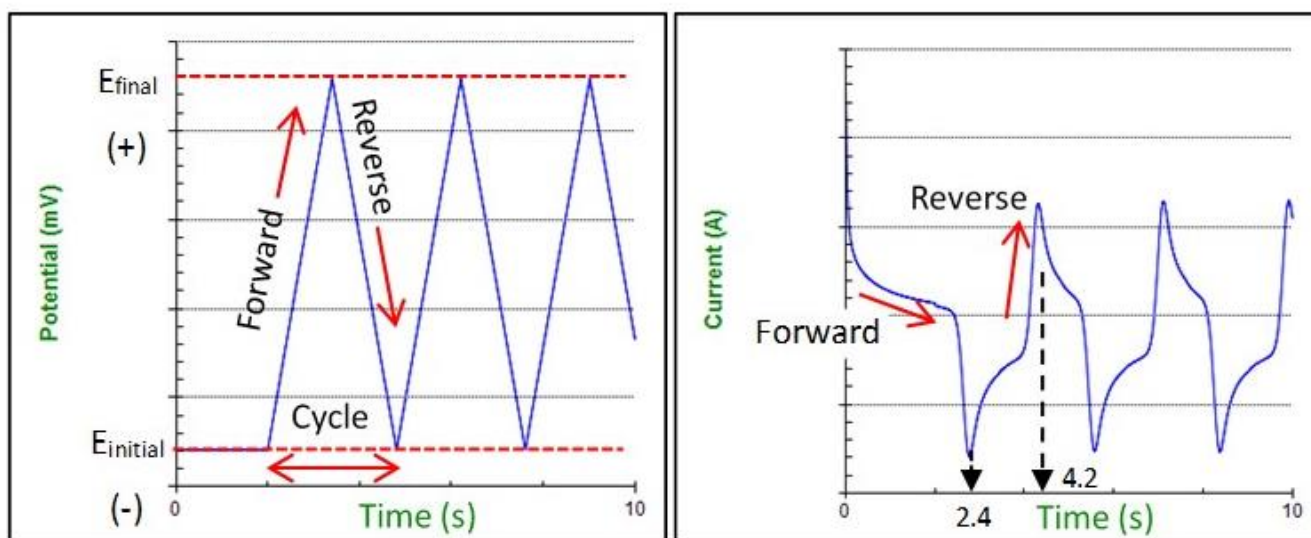
**Figure 1** (a) The potential as a function of time, (b) the resulted current as a function of time

The typical linear sweep voltammogram of ferricyanide was obtained as shown in Figure 2 which is current as a function of potential. At onset potential around 0 mV, ferricyanide was started to be oxidized and got the maximum anodic current ( $I_{\text{pa}}$ ) at around 165 mV ( $E_{\text{pa}}$ ).



**Figure 2** The typical Linear sweep voltammogram of ferricyanide

Moreover, cyclic voltammetry, applied potential was scanned forward to the final potential and then reverse scanned to the initial potential and thus forms a triangular potential waveform cycle as shown in Figure 3(a). Figure 3(b) represents the obtained current as a function time with applied cyclic potential sweep, the ferricyanide started to be oxidized at around 2.2 second and got maximum current at around 2.4 second, and in the opposite scanning, the reduced reaction was started at around 4 second and got maximum at around 4.2 second within a complete cycle. With these information, the electron transfer rate can be calculated and analyzed for qualification and quantification of the analyte.

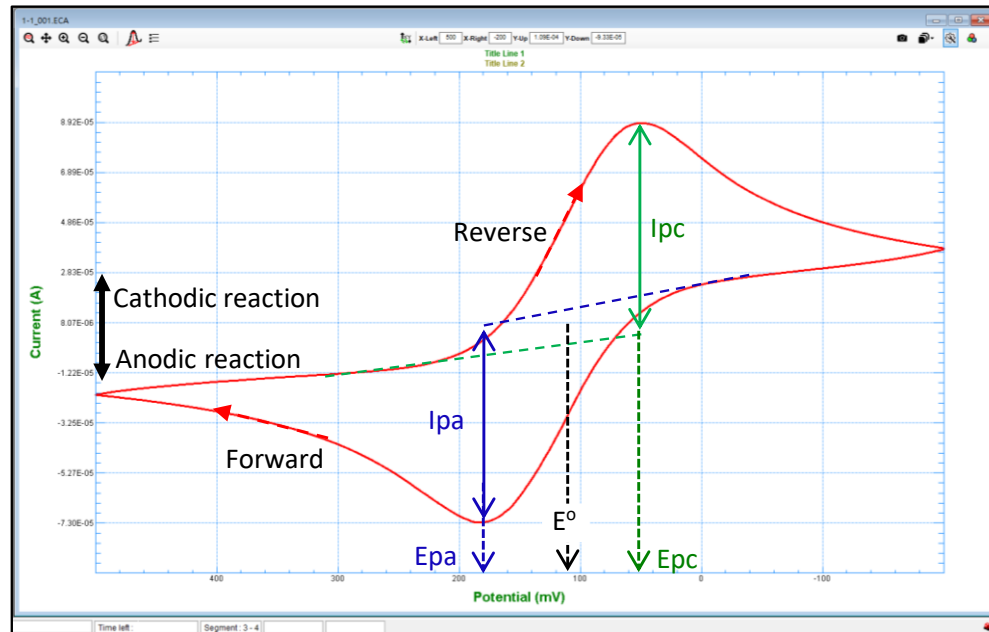


**Figure 3** (a) The potential as a function of time, (b) The current as a function of time.

#### References

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

Figure 4 represents the typical cyclic voltammogram for redox process of ferricyanide. In the forward scan, it goes with the anodic reaction and get the anodic current ( $I_{pa}$ ) and anodic potential ( $E_{pa}$ ), in the opposite way, reverse scan, it belongs to the cathodic reaction and obtains the cathodic current ( $I_{pc}$ ) and cathodic potential ( $E_{pc}$ ) of the analyte. Anodic reaction is an oxidizing reaction which the analyte lose one electron or more to the electrode for analysis. On the other hand, the cathodic reaction means the analyte gets one electron or more from the electrode. However, forward scan can be anodic or cathodic, it depends on the direction of scan, and so does the reverse scan.

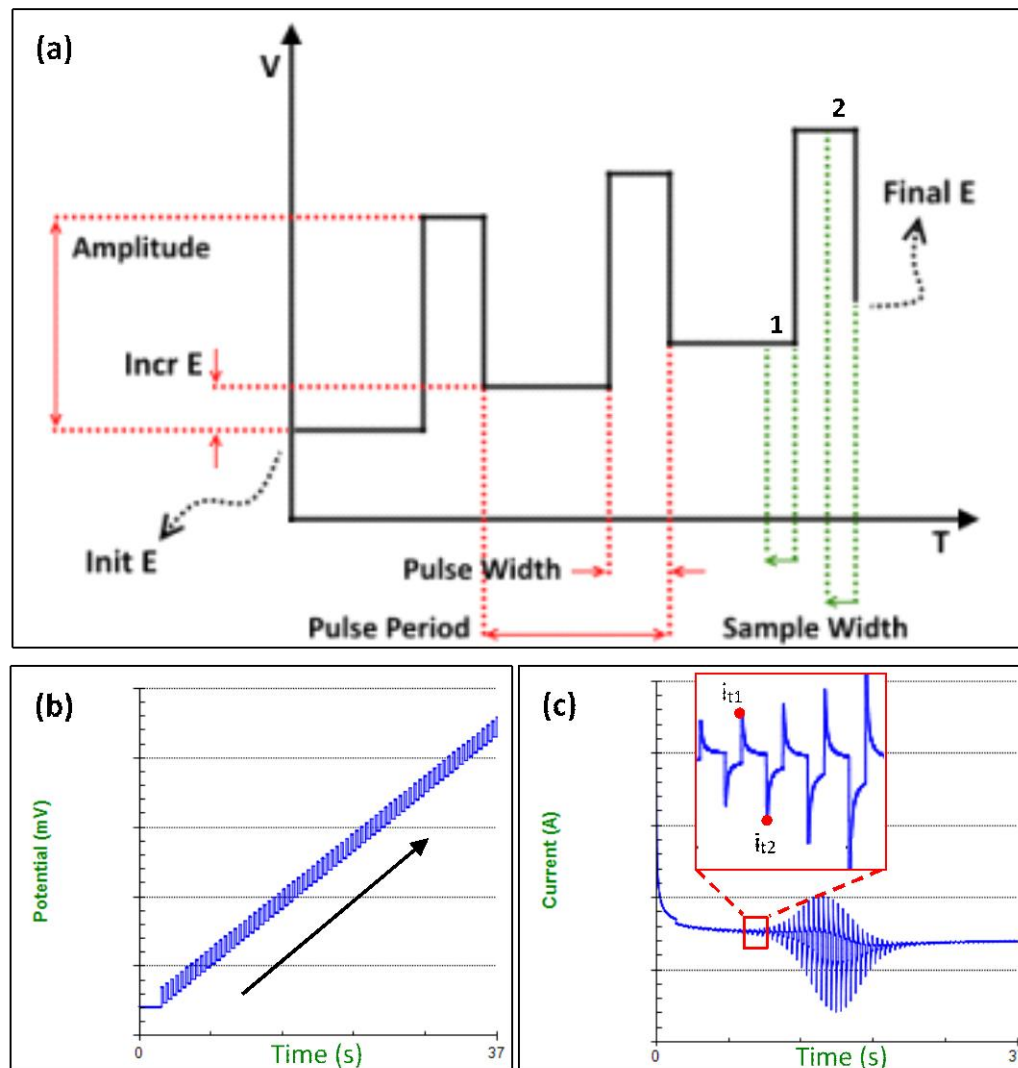


**Figure 4** Typical cyclic voltammogram

#### References

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

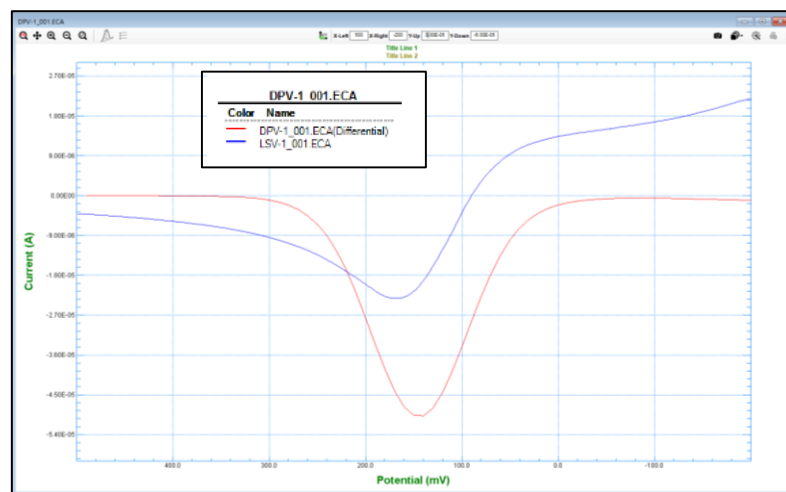
## 1.2.2 Differential Pulse Voltammetry



**Figure 5** (a) Waveform of Differential Pulse Voltammetry, (b) The differential pulse potential as a function of time, (c) The measured current as a function of time.

Sir Geoffrey Barker, the inventor of Pulse Voltammetry, gives us the technique to measure trace level of analyte by decreasing the charging current and thinner diffusion layer. The differential pulse voltammetry named from the DIFFERENCE of two sampling current which are the first sample point before the pulse application and another point around 40ms late of the pulse.

Figure 5 (a, b) represents the detailed description of waveform of differential pulse voltammetry that gives the fixed amplitude of pulses with an increasing linear potential sweeping. In Figure 5 (c), the current is sampled twice, which are  $i_{t1}$  and  $i_{t2}$ . Therefore,  $i_{t1}$  is subtracted from  $i_{t2}$  to being the current difference and then to be plotted as a function of potential as shown in Figure 6. It is clearly that the signal of DPV is larger than the signal of LSV in the presence of 30 mM ferricyanide and can be used to quantify the analyte with low detection limit.

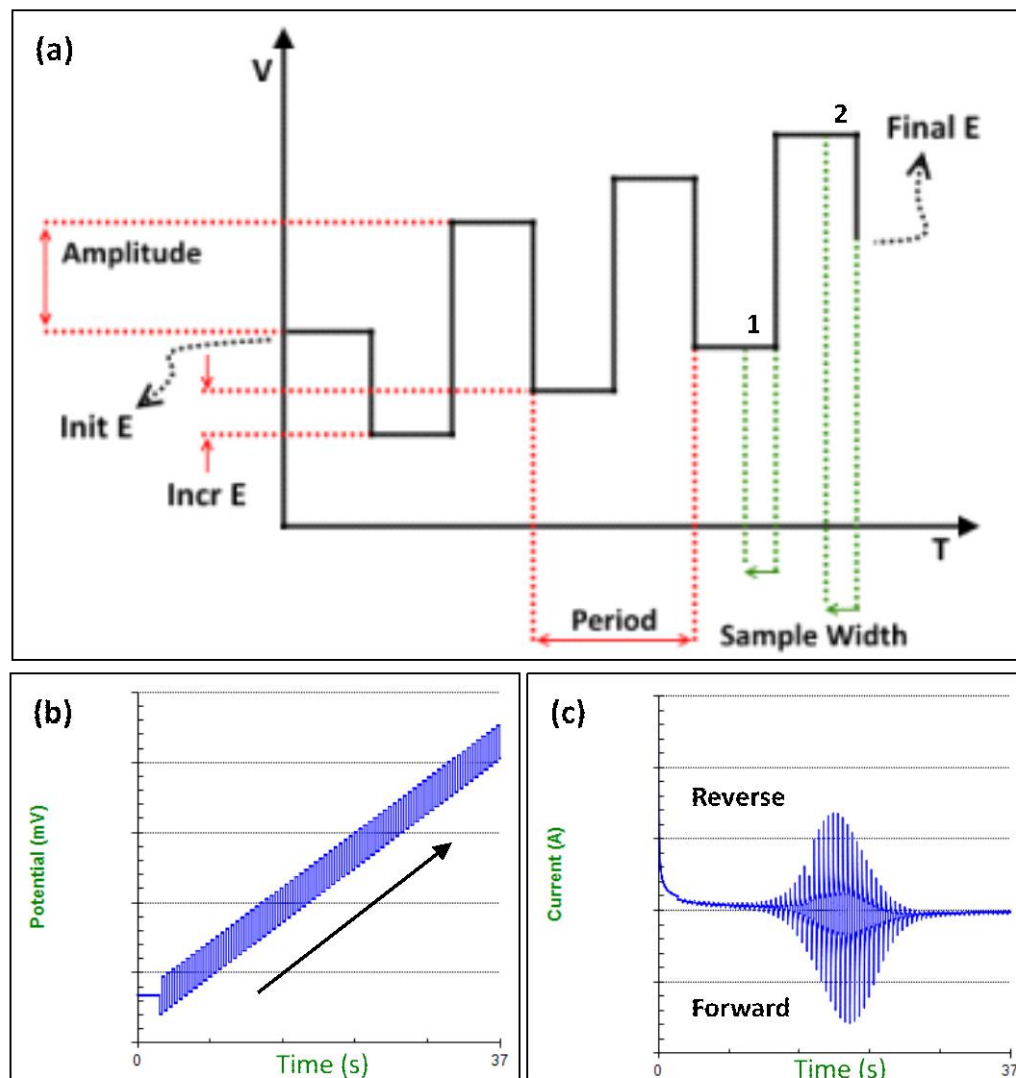


**Figure 6** Differential pulse (red) and linear sweep (blue) voltammogram for 30 mM Ferricyanide.

#### References

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

## 1.2.3 Square Wave Voltammetry



**Figure 7** (a) Waveform of Square Wave Voltammetry, (b) The square wave potential as a function of time, (c) The measured current as a function of time.



As illustrated in Figure 7 (a, b), the symmetrical square wave potential is applied to the electrode as a function of time with a twice larger amplitude. The measured current is also sampled twice as well as DPV, one is for forward pulse and the other is for reverse pulse. (see Figure 7 (c)) The difference between forward and reverse gives a current plot and resulting its sensitivity is higher than the differential pulse voltammetry in a reversible redox system, in which the signal of SWV is larger than the signal of DPV in the presence of 30 mM ferricyanide as shown in Figure 8. Moreover, the advantage of SWV is its fast scan rate which is equal frequency multiplied increasing potential.

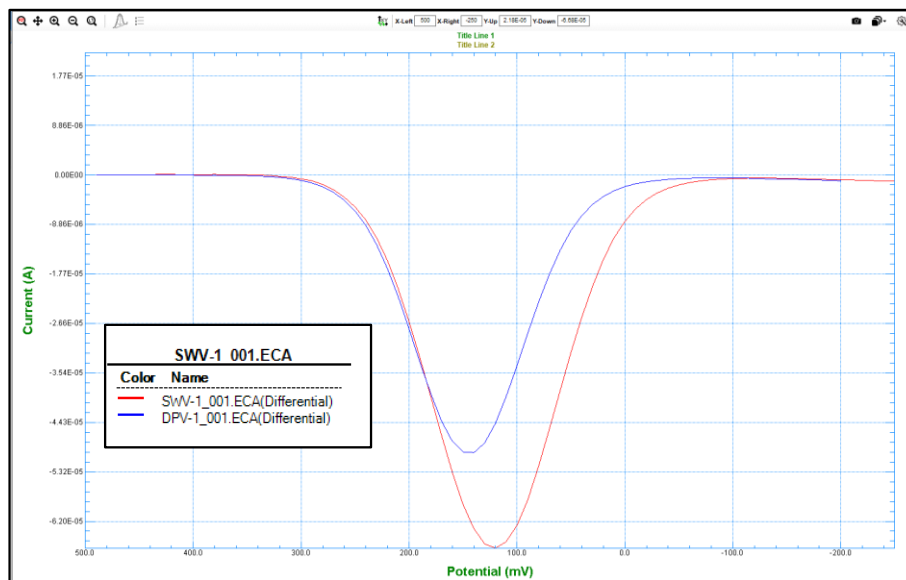


Figure 8. Square wave (red) and Differential pulse (blue) voltammogram for 30 mM Ferricyanide.

#### References

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

## 1.2.4 Amperometry

Amperometry is one of the most employed method in electroanalysis. It is applied a fixed potential ( $E_p$ ) and measure the current as a function of time as illustrated in Figure 9. It is widely used in the quantification of biomolecule in point of care device such as glucose sensor device.

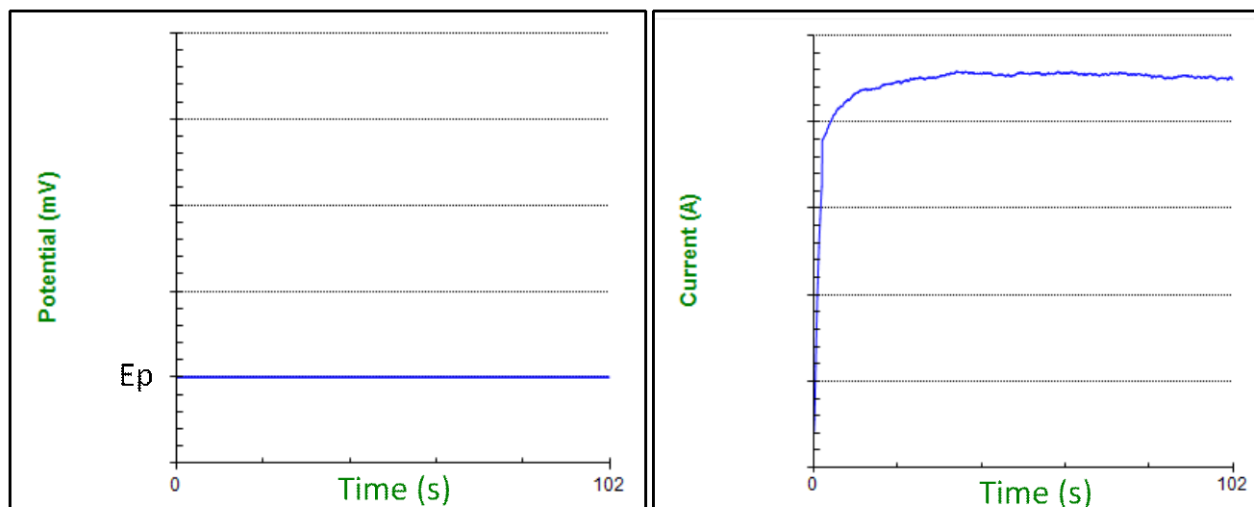


Figure 9. (a) the waveform of amperometry, (b) the measured current as a function of time.

### References

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

## 1.2.5 Open circuit potential

Open circuit potential is used to measure the potential difference between two terminals of a device which the circuit is not closed. (i.e., no current flow through.)

### References

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