Comparison between staircase cyclic voltammetry and cyclic voltammetry, linear scan

The staircase method for cyclic voltammetry is widely used in digital instruments, due to the discrete nature of digital electronics. Moreover the electrical double layer contribution to the current, or the charging current, is reduced if the duration of the step is sufficiently long. This results in data that can be treated as originating from faradaic processes only. The Autolab electrochemical instruments and its software normally use the staircase method for cyclic voltammetry measurements. Cyclic voltammetry with true analog sweep (called cyclic voltammetry, linear scan) is available through the use of SCANGEN module.

Figure 1, shows an example of a waveform for a staircase experiment. The moment at which the current is measured (designated by the value of α) can be specified; for α=0.25 the current is sampled at one quarter of the total step duration, for α=1 the current is sampled at the end of the step, etc. In order to improve the signal to noise ratio, the sampling of the current is done during a certain time interval, if possible during on net cycle (20 or 16.6 ms).

When kinetic processes are studied, the difference between the staircase and the linear sweep method is expected not to be very large. M. Seralthan and R.A. Osteryoung (J.Electroanal. Chem. 222, 69(1987)) have made a theoretical comparison between normal staircase voltammetry and cyclic voltammetry, linear scan. They showed that similar results could be obtained when the current is measured at the right moment during the step; for a reversible system the current should be sampled at one quarter of the total step duration. So, for those involved in the research of electrochemical kinetics, staircase voltammetry is a good alternative for cyclic voltammetry, linear scan.

The story is different for time dependent processes like Under Potential Deposition (UPD), Electrical double layer effects and Hydrogen adsorption on Pt. In these cases the above described (normal) staircase method fails. This is because these phenomena take place at the beginning of a step and vanish when the current is sampled.

Autolab instruments and software also offer a staircase method, which is able to record these fast phenomena. In this method the analog current integrator is used. The integrator is reset at the beginning of each step. Subsequently, the integrated current or charge is sampled at the end of each step. By dividing the charge value by the step duration a value for the (pseudo) current is obtained.

Autolab instruments and software offer cyclic voltammetry, linear scan, which should give the same result as the current integration method.

Figure 2 shows a voltammogram of polycrystalline Au in perchloric acid. The three different methods are indicated with SV (Staircase Voltammetry), LSV (Cyclic Voltammetry, Linear scan) and SV-CI (Staircase Voltammetry-Current Integration).

Figure 3 shows the double layer region of the same curve. It is here clearly visible that charging currents due to the double layer capacitance are suppressed when the staircase method is used. Furthermore cyclic voltammetry, linear scan and current integration voltammetry give the same response.

Figure 4 shows the voltammogram of a Pt electrode in sulphuric acid. The difference between SV and the other two methods is clearly visible in the hydrogen adsorption region. This region is suppressed in the case of staircase voltammetry because the hydrogen adsorption is so fast that the process is ended before the end of the step. One therefore only measures the end of the adsorption process. For a normal kinetic process, the differences between the three methods are small.

Figure 1: Waveform for staircase voltammetry and voltemmetry, linear scan. Value of alpha denotes the moment of sampling

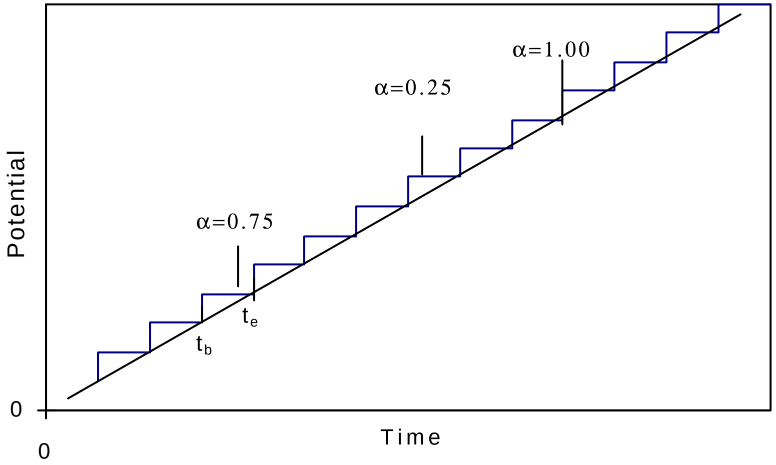

Figure 2: Full CV for polycrystalline Au, measured with three different methods.

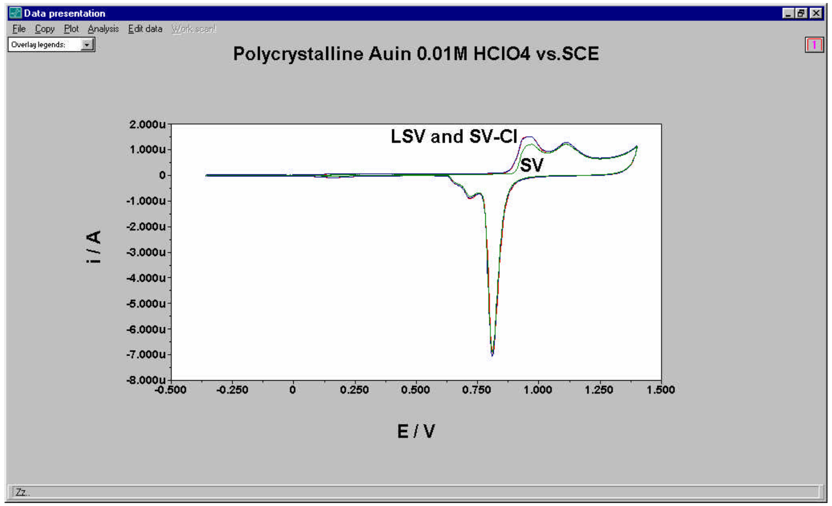

Figure 3: Same as Figure 2 but zoomed into the double layer region.

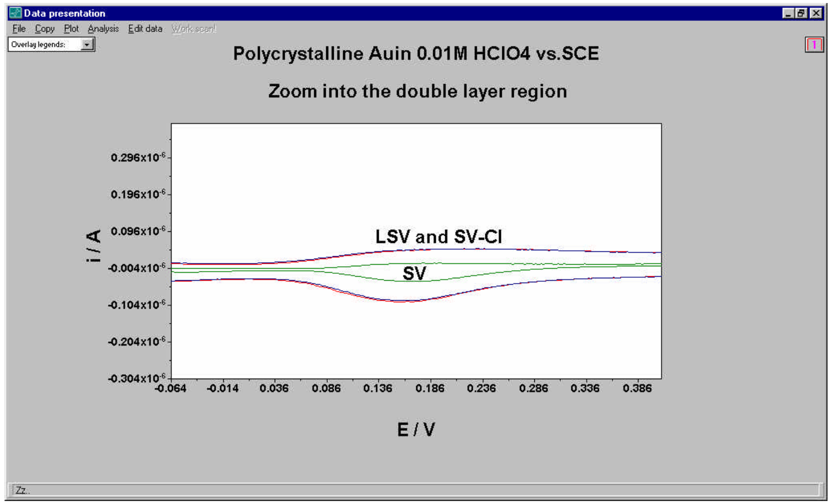

Figure 4: CV of Pt electrode in sulphuric acid.