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Autolab Application Note EC12

Different approaches for capacitance measurements

Keywords

SCAN250, capacitor, charge, linear scan, staircase scan, step potential, current integrator, FI20, permittivity, chrono amperometry, electrochemical impedance spectroscopy, EIS.

Introduction

The relative permittivity ε_r, also known as dielectric constant, is of great importance in materials characterization. It can be defined as the ratio between the amount of electrical energy stored in a material and the amount of electrical energy stored in the vacuum (hence the term relative). It is a frequency-dependent quantity but, at low frequencies, ε_r becomes constant and is referred as the static relative permittivity.

One of the easiest way to obtain the relative permittivity is to calculate it from capacitance values. Different formulas hold for different capacitor geometries. In the case of a parallel plate capacitor, the capacitance C and the relative permittivity ε_r are related according to the following formula:

$$C = \varepsilon_0 \varepsilon_r \frac{A}{d}$$

where A is the overlap area of the two plates, d is the distance between the plates and ε_0 is the vacuum permittivity, 8.854 pF m^{-1}.

Furthermore, if the charge q varies linearly with the potential V, the slope of the line q vs. V gives the capacitance C:

$$q = CV$$

One of the most common methods is to sample the charge, during a potential scan.

Experimental

In this application note, five techniques are compared. Three techniques are based on potential sweep, i.e., staircase sweep, linear sweep and current integration. The other two techniques are chrono amperometry and electrochemical impedance spectroscopy (EIS).

All the measurements are carried out with the Autolab PGSTAT204, fitted with the FRA32M impedance analyzer and the onboard current integrator, except for the linear scan measurements, which is carried out with a PGSTAT302N fitted with the SCAN250 module.

The measurements are performed on two electrical circuits provided by the Autolab dummy cell (labelled *c* and *d*, respectively).

Position *c* of the dummy cell, used for the impedance spectroscopy measurements, corresponds to a R(RC) circuit, as shown in Figure 1.

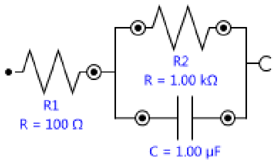

Figure 1 – The electrical circuit *c*

Position *d* of the dummy cell, used for all the measurements, corresponds to a RCR circuit, as shown in Figure 2.

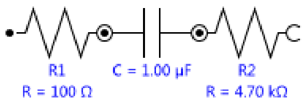

Figure 2 – The electrical circuit *d*

The connections to the two circuits provided by the Autolab dummy cell are shown in Figure 3.

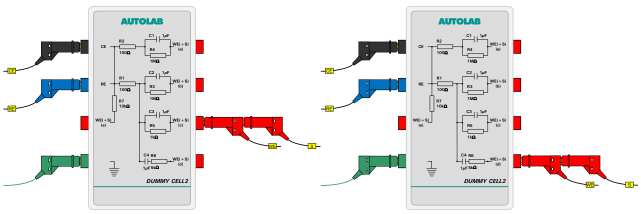

Figure 3 – Connections to the Autolab dummy cell (circuit *c* and *d*)

Staircase and linear scan

Two types of scans are available, a staircase scan and a true linear scan. For a description of both methods, the reader is invited to consult the application note Comparison between Staircase Cyclic Voltammetry and Cyclic Voltammetry Linear Scan.

In both cases, a potential sweep voltammetry is set. Each scan consists of sweeping the potential between 0 V and 1 V, with a scan rate of 0.1 V/s. The potential, current and charge are sampled.

Figure 4 shows the charge vs. potential plot of a staircase scan.

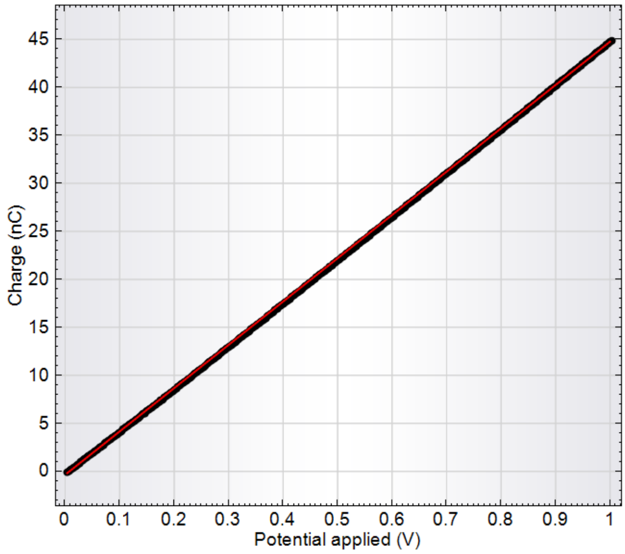

Figure 4 – Charge vs. potential, in the case of a staircase scan, measured on dummy cell *d*

Figure 5 shows the charge vs. potential plot of a true linear scan.

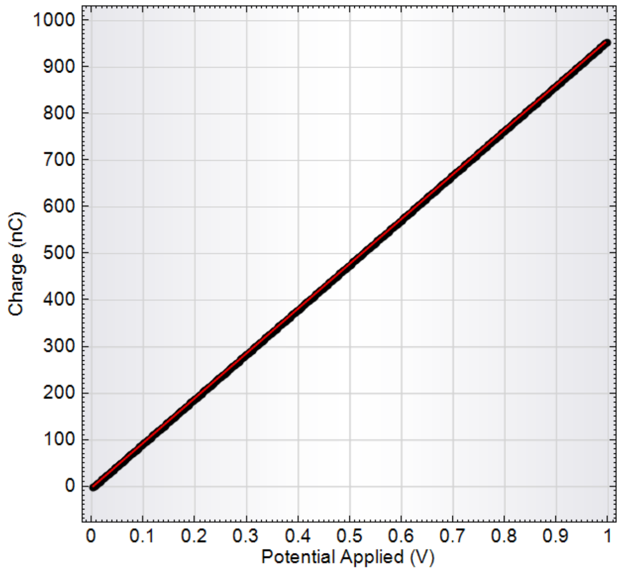

Figure 5 – Charge vs. potential, in the case of a true linear scan, measured on dummy cell *d*

For each plot, the capacitance is calculated from the slope of the linear regression. In the case of the staircase scan, Figure 4, the capacitance is 45.1 nF. In the case of the true linear scan, Figure 5, the slope of the regression gives a capacitance of 961 nF.

Current integration cyclic voltammetry

In the case of the current integration cyclic voltammetry, the charge, together with the potential and current are sampled. The same regression and calculations of the previous experiments hold. In this application note, the current integrator of a PGSTAT204 is used.

Figure 6 shows the charge vs. potential plot, measured with the current integration cyclic voltammetry method.

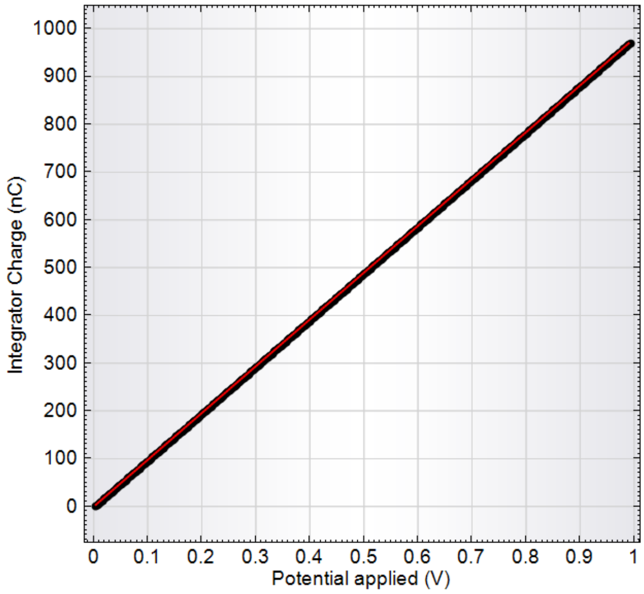

Figure 6 – Charge vs. potential, in the case of the current integrator, measured on dummy cell *d*

The capacitance calculated from the slope of the charge vs. potential plot is 980 nF, which is in very good agreement with the result obtained using the linear scan cyclic voltammetry method.

Chrono amperometry

In the chrono amperometry, a potential profile composed of three steps is applied (see Figure 7):

- 0 V for 100 ms;
- 1 V for 100 ms;
- 0 V for 100 ms.

The current is recorded using an interval time of 100 µs.

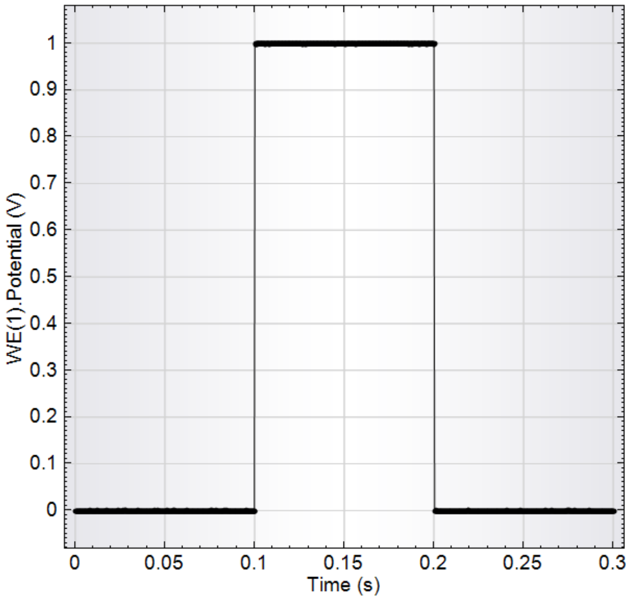

Figure 7 – Potential vs. time profile used for the chrono amperometry measurement

In Figure 8, the plot of the current vs. time is shown, where the charging (at 0.1 s) and discharging (at 0.2 s) can be seen.

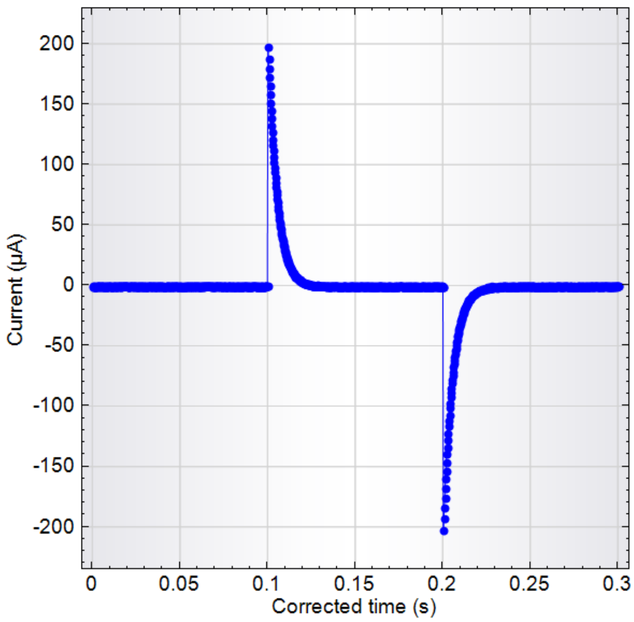

Figure 8 – Current vs. time plot measured with chrono amperometry on dummy cell *d*

The discharge occurs according to the following equation:

$$i = \frac{E_{Step}}{R} e^{\left(-\frac{t}{RC}\right)}$$

Where the current i is a function of the time t and it depends on the potential step E_{Step}, the uncompensated resistance R and the capacitance C.

In order to calculate the capacitance, the first transient in Figure 8 is selected and the corrected time is used (starting from t = 0).

The current decay is linearized by calculating the natural logarithm of the current. As the following equation shows, the intercept at t = 0 gives the value of the uncompensated resistance, R, and the slope provides the value of the capacitance, C. In this case, E_{Step} corresponds to 1 V.

$$\ln(\mathrm{i}) = \ln\left(\frac{E_{Step}}{R}\right) - \frac{t}{RC}$$

In Figure 9, the plot of the linearized current vs. discharge time is shown (blue dots), together with the regression line (black line), with the following equation:

$$y = -8.50 - 209.02t$$

Resulting in a R value of 4.92 kΩ and a C value of 973 nF.

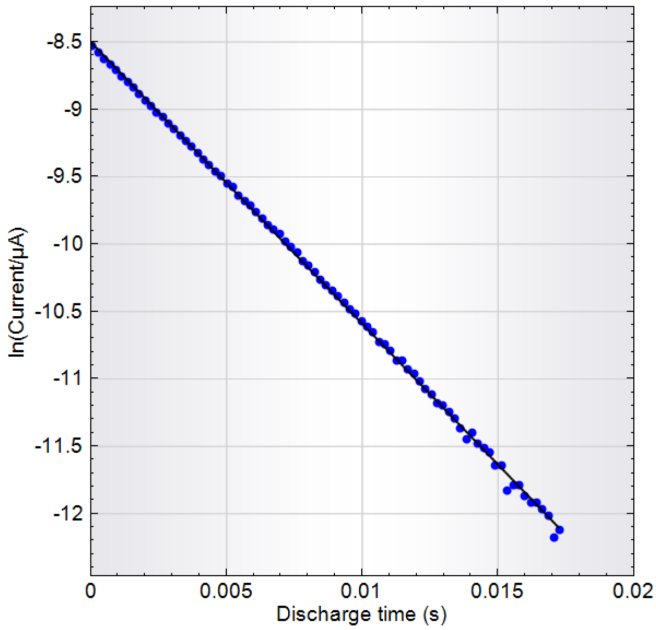

Figure 9 – Linearized discharge current

Electrochemical impedance spectroscopy (EIS)

The advantage of using the EIS is that it is possible to calculate the capacitance as function of the frequency. For both the series and parallel configuration, the potentiostatic impedance spectrum is collected, with the frequency range from 100 kHz to 100 mHz, and a potential amplitude of 10 mV RMS, collecting 10 frequencies per decade.

Regarding the series configuration, the Nyquist plot and the relative equivalent circuit are shown in Figure 10.

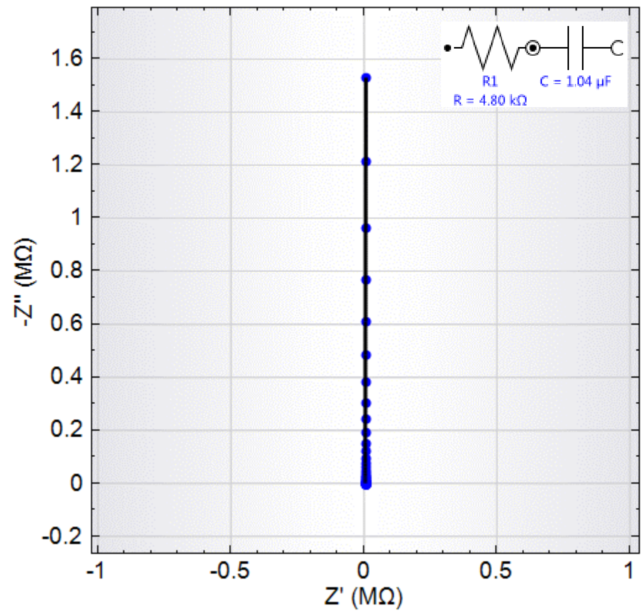

Figure 10 – Nyquist plot (blue dots) and the fit (black line) for the RC configuration, together with the equivalent circuit, measured on dummy cell *d*

In this case, the fit gave a $R1$ of 4.8 kΩ and a C value of 1.04 µF.

Similarly, the parallel configuration R1(R2C) has been used, for comparison. The resulting Nyquist plot and the relative equivalent circuit are shown in Figure 11.

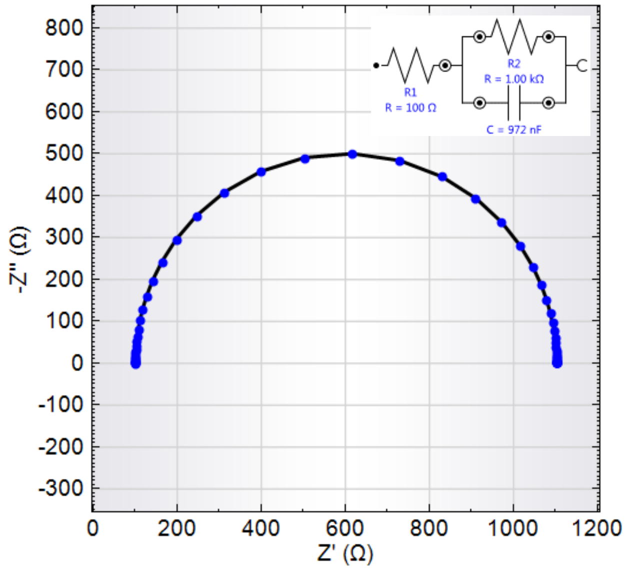

Figure 11 – Nyquist plot (blue dots) and the fit (black line) for the R(RC) configuration, together with the equivalent circuit, measured on dummy cell *c*

In this case, the fit gives a $R1$ of 100 Ω, a $R2$ value of 1 kΩ, and a C value of 972 nF.

Summary

The capacitance values obtained with the experiments are summarized in Table 1.

Experiment	Capacitance (nF)
Staircase Scan	45.1
Linear Scan	961
Current Integrator	980
Chrono amperometry	972
EIS – RC	1040
EIS – R(RC)	973

Table 1 – Capacitance values extracted from the experiments

Since the value of the capacitor used is 1 µF with a tolerance of 5%, i.e. 1 µF ± 50 nF, the expected value lies between 1.05 µF and 950 nF. Therefore, the values found with the true linear scan, the current integrator, the chrono amperometry and with the impedance spectroscopy can be considered valid.

Conclusion

The capacitance is an important quantity, used to calculate the relative permittivity of dielectric materials. This application note shows that a true linear scan, rather than a staircase scan, should be used in order to obtain a reliable capacitance value, since the staircase scan neglects the capacitive current. Other methods like the current integrator, the chrono amperometry and the electrochemical impedance spectroscopy give also valid results.

Date

26 August 2014