

Application Area: Fundamental

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 (F) and the relative permittivity ϵ_r are related according to the following Equation

$$C = \epsilon_0 \epsilon_r \frac{A}{d} \quad 1$$

Where A (m^2) is the overlap area of the two plates, d (m) is the distance between the plates and ϵ_0 ($= 8.854E - 12 F m^{-1}$) is the vacuum permittivity.

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

$$q = CV \quad 2$$

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

Experimental

In this application note, five techniques have been 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 were carried out with the Metrohm Autolab PGSTAT204, fitted with the FRA32M impedance analyzer and the onboard current integrator, except for the linear scan measurements, which were carried out with a PGSTAT302N fitted with the SCAN250 module.

The dummy cell delivered with the pgstats has been tested in the position d (Figure 1-1), in all the experiments, and in the position c (Figure 1-2) and d for the impedance measurements. The reference and counter electrode leads have been connected to the respective inputs and the working electrode with the sensor leads.

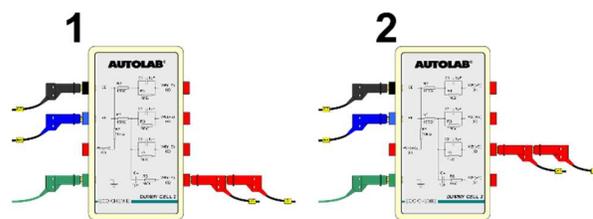


Figure 1 – The dummy cell, position d (1) and c (2)

The position d is composed of a series configuration [R1CR2], Figure 2-1, where $R1 = 100 \Omega$, $C = 1 \mu F$ and $R2 = 4.7 k\Omega$ (even if the reported value is $5 k\Omega$); the position c is a parallel [R1(R2C)] configuration, Figure 2-2, with $R1 = 100 \Omega$, $R2 = 1 k\Omega$ and $C = 1 \mu F$.

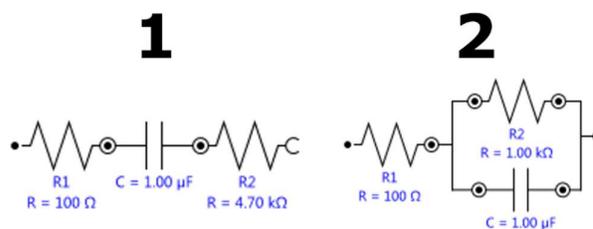


Figure 2 – Equivalent circuits corresponding to the d configuration (1) and the c configuration (2) of the dummy cell.

Staircase and linear scan

Two types of scans are available, a staircase scan and a true linear scan. In both cases, a potential sweep voltammetry was set. The scan consisted of sweeping the potential between 0 V and 1 V, with a scan rate of 0.1 V/s. For the

staircase scan, the step size was 2.44 mV. The potential, current and charge have been sampled.

Figure 3 shows the charge versus potential plot of a staircase scan.

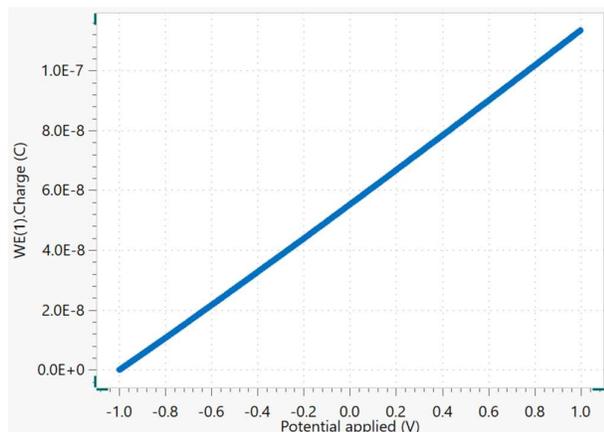


Figure 3 – Charge vs. potential, in the case of a staircase scan, measured on dummy cell d.

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

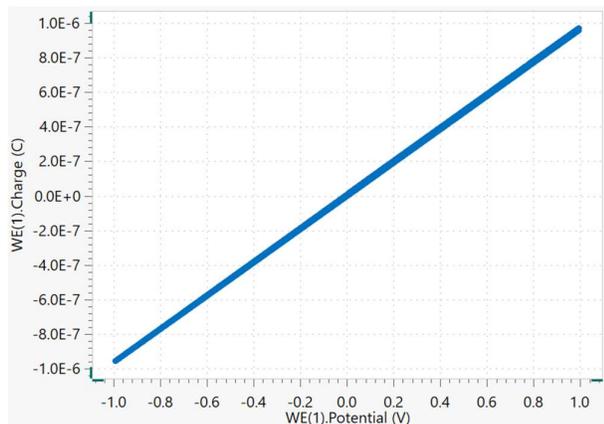


Figure 4 – Charge vs. potential, in the case of a true linear scan, measured on dummy cell d.

For each plot, the capacitance has been calculated as the slope of the linear regression, according to Equation 2. In the case of the staircase scan in Figure 3, the capacitance is 55.6 nF. In the case of the true linear scan in Figure 4, the slope of the regression gives a capacitance of 967 nF.

Current integrator

In the case of the current integrator, the integrator charge was sampled, together with the potential and current. The 10 μA

current range and a 10 ms integration time were chosen. The same regression and calculations of the previous experiments hold. In this application note, the current integrator of a PGSTAT204 was tested.

Figure 5 shows the charge versus potential plot, measured with the current integrator on. For a description of the current integrator, please refer to the Appendix, at the end of this application note.

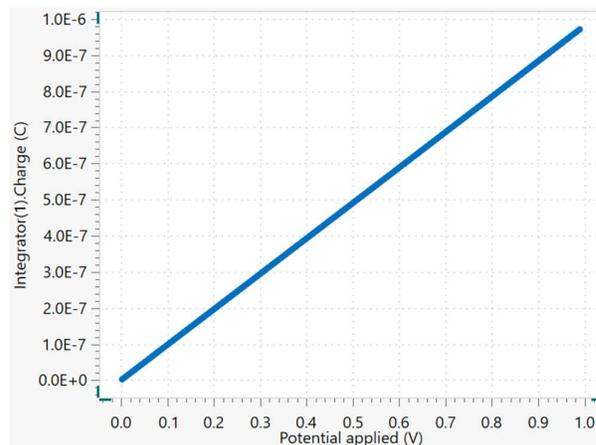


Figure 5 – Charge vs. potential, in the case of the current integrator, measured on dummy cell d.

In addition, the capacitance has been calculated as the slope of the charge vs. potential plot, resulting in 980 nF.

Chrono Amperometry

In the Chrono Amperometry, the current has been sampled, when a potential profile composed of three steps was applied (Figure 6):

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

The fast option has been chosen, in order to record enough number of points. The interval time was set on 100 μs .

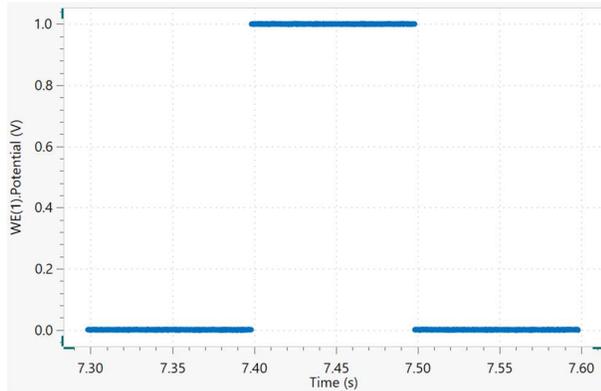


Figure 6 – Potential vs. time profile used for the chrono amperometry measurement.

In Figure 7, the plot of the current versus time is shown, where the charging (at 0.1 s) and discharging (at 0.2 s) are present.

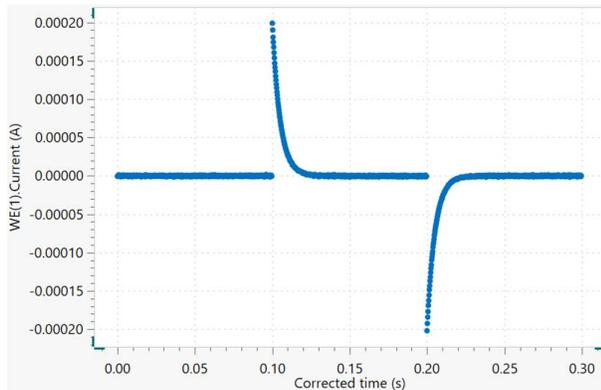


Figure 7 – Current vs. time plot measured with chrono amperometry on dummy cell d.

The discharge occurs according to the following equation,

$$i = \frac{E_{step}}{R_u} \exp\left(-\frac{t}{R_u C}\right) \quad 3$$

Where the current i (A) is a function of the time t (s) and it depends on the potential step E_{step} (V), the uncompensated resistance R_u (Ω) and the capacitance C (F).

In order to calculate the capacitance, the first peak in Figure 7 has been selected and the corrected time has been used (starting from $t = 0$).

The linearization of the decay was done by calculating the natural logarithm of the current, Equation 4.

$$\ln(i/A) = \ln\left(\frac{E_{step}}{R_u}\right) - \frac{t}{R_u C} \quad 4$$

Here, the intercept at $t = 0$ s gives the value of the uncompensated resistance R_u , and the slope the capacitance C . In this case, $E_{step} = 1$ V.

In Figure 8, the plot of the linearized current versus the corrected discharge time is shown.

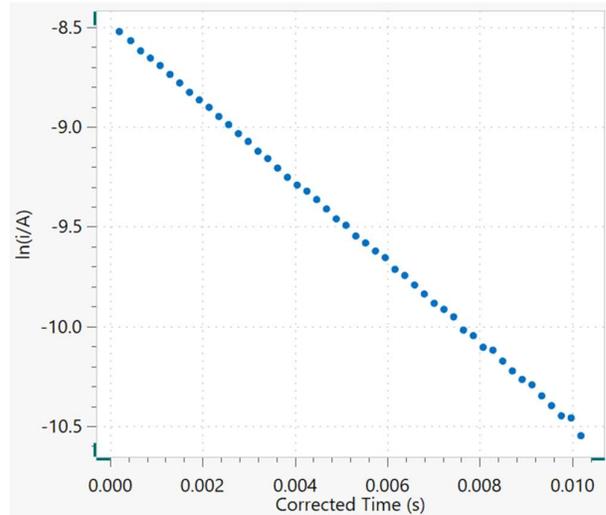


Figure 8 – Potential vs. Corrected time, in the case of the current integrator

The regression line applied to the plot of Figure 8 results in the following Equation

$$\ln(i/A) = -8.48 - 199.8 t \quad 5$$

For calculating the uncompensated resistance R_u , the intercept at $t = 0$ s in Equation 4, is equal to the intercept at $t = 0$ s in Equation 5:

$$\ln\left(\frac{E_{step}}{R_u}\right) = -8.48$$

$$\ln\left(\frac{R_u}{E_{step}}\right) = 8.48 \quad 6$$

$$R_u = E_{step} \exp(8.48)$$

Resulting in R_u 4.802 k Ω .

Regarding the calculation of the capacitance C , the slope in Equation 4 is equal to the slope of Equation 5:

$$-\frac{t}{R_u C} = -199.8 t$$

$$C = \frac{1}{R_u \cdot 199.8}$$

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Resulting in C 1.04 μF .

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 has been collected, with the frequency range from 100 kHz to 100 mHz, with a potential amplitude of 10 mV RMS, collecting 10 frequencies per decade.

Regarding the series configuration (Figure 2-1), the Nyquist plot is shown in Figure 9.

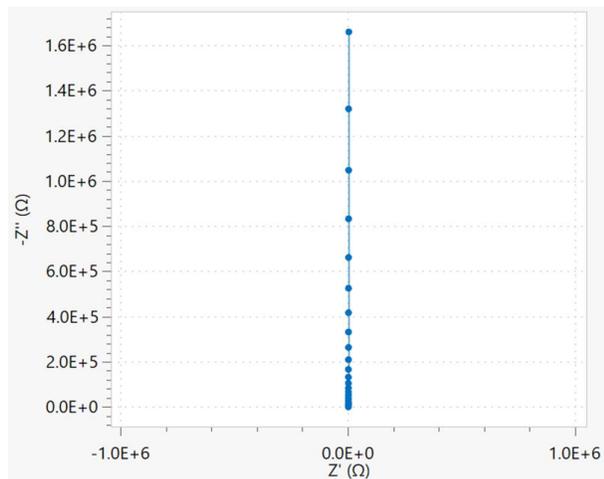


Figure 9 – Nyquist plot (blue dots) and the fit (blue line) for the [RC] configuration, measured on dummy cell d.

In this case, the fit gave $R_1 = 4.84 \text{ k}\Omega$ and $C = 957 \text{ nF}$.

Similarly, the parallel configuration [R1(R2C)] (Figure 2-2) was measured, for comparison. The resulting Nyquist is shown in Figure 10.

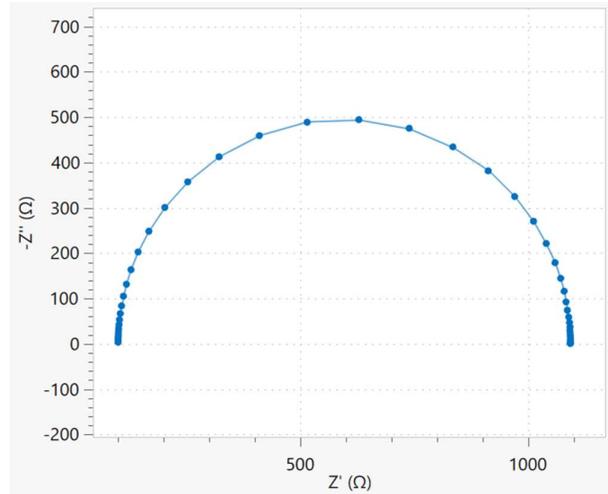


Figure 10 – Nyquist plot (blue dots) and the fit (black line) for the [R1(R2C)] configuration, together with the equivalent circuit, measured on dummy cell d.

In this case, the fit results were $R_1 = 100 \Omega$; $R_2 = 993 \Omega$ and $C = 945 \text{ nF}$.

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

Table 1 – Capacitance values extracted from the experiments.

	Capacitance (nF)
Staircase Scan	55.6
Linear Scan	967
Current Integrator	980
Chrono amperometry	1040
EIS – [R1C]	957
EIS – [R1(R2C)]	945

Since the value of the capacitors used is $1 \mu\text{F}$ with a tolerance of 5%, i.e., $1 \mu\text{F} \pm 50 \text{ nF}$, an acceptable value lies between $1.05 \mu\text{F}$ and 950 nF . Therefore, the values found with the true linear scan, the current integrator, the chrono amperometry and with the electrochemical impedance spectroscopy measurements 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

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For more information

Additional information about this application note and the associated NOVA software procedure is available from your local Metrohm distributor. Additional instrument specification information can be found at www.metrohm.com/en/products/electrochemistry.

Appendix – current integrator

The current integrator is composed of a capacitor placed in the control loop of the working electrode, where the current is measured. This module is embedded as default in PGSTAT101 and PGSTAT204. In the case of the N series instruments, the current integrator can be performed with the FI20 module. A drawing of a current integrator is shown in Figure 11.

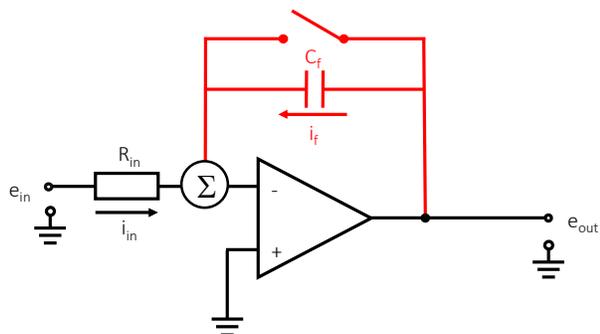


Figure 11 – the current integrator is a capacitor placed after the working electrode. The switch on top is used to discharge the capacitor before each measurement.

The output voltage is proportional to the integrated input current, i.e., the charge stored in the capacitor C_f .

$$e_{out} = -\frac{1}{C_f} \int i_{in} dt$$