Electronic Supplementary Information (ESI)

Pencil Drawn Paper Based Supercapacitors

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Electronic Supplementary Information

A systematic approach to characterising the capacitance of an electrode pair in parallel circuit with a capacitor is presented here. In order to best describe the benefit of this approach, the principles of capacitor theory should be understood. A specific example can be used, with three capacitors, which illustrates how utilising a parallel circuit can improve the interpretation of results. In this example we consider three capacitors of capacitance C_1, C_2 and C_3. We will assume that the capacitor C_1 is the supercapacitor such that $C_1 = C_{supercapacitor}$. The first case where the capacitors are connected in parallel, as shown in ESI Figure 1. In this case the potential across the capacitors is the same:

$$V = V_2 = V_3 = V_{Supercapacitor} \tag{1}$$

and as such the total charge is distributed equally across the capacitors:

$$Q = Q_2 = Q_3 = Q_{Supercapacitor} \tag{2}$$

and consequently:

$$C_{total}V = C_2V_2 + C_3V_3 + C_{Supercapacitor}V_{Supercapacitor} \tag{3}$$

but from ESI equation 1) we have:

$$C_{total}V = C_2V + C_3V + C_{Supercapacitor}V \tag{4}$$

and finally

$$C_{total} = C_2 + C_3 + C_{Supercapacitor} \tag{5}$$

In this example, the total capacitance of the parallel circuit is the sum of all the capacitances of each of the parallel branches.

The second case is where there are three capacitors in series as shown in ESI Figure 1B. In this case the potential is split between each of the components in series:

$$V = V_2 + V_3 + V_{Supercapacitor} \tag{6}$$

and

$$V = V_2 + V_3 + V_{Supercapacitor} \tag{7}$$

therefore

$$\frac{Q}{C_{total}} = \frac{Q}{C_2} + \frac{Q}{C_3} + \frac{Q}{C_{supercapacitor}} \tag{8}$$

and finally

$$\frac{1}{C_{total}} = \frac{1}{C_2} + \frac{1}{C_3} + \frac{1}{C_{supercapacitor}} \quad (8)$$

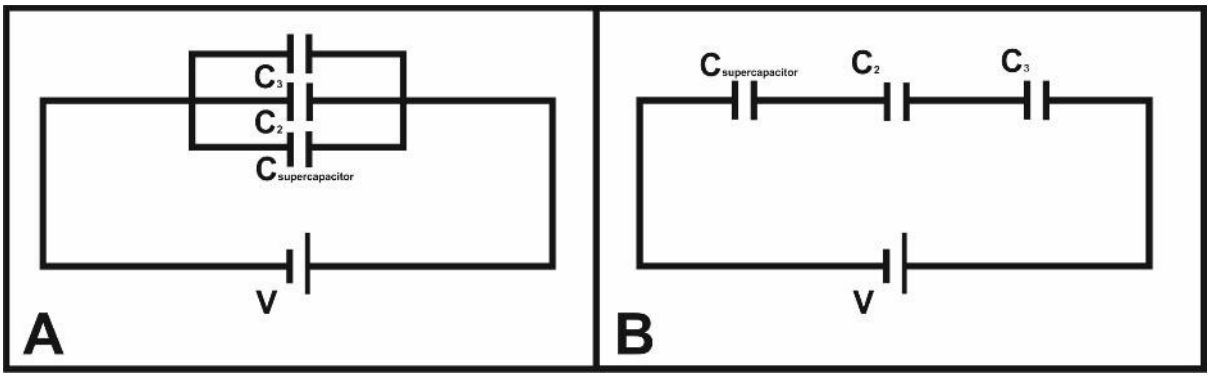
In this case the total capacitance of the series circuit is the sum of the inverse capacitances of the components.

If we consider the effect of this comparison on the analysis of the capacitive properties of the supercapacitor we can see the benefit of analysing the properties in a circuit of know capacitance. ESI Figure 2 shows the various arrangements for analysis of the supercapacitor in parallel with a 100 μF capacitor. Either a single 100 μF capacitor is utilised in parallel show in ESI Figure 1B or a variable capacitor system is set to 100 μF in parallel, shown on ESI Figure 1A. The effect this has on the observed charging cycle and the interpretation of the *dV/dt* are shown in ESI Figure 1C. As a commercial grade capacitor has a nominally linear response, the resulting curve is a combination of a linear curve and the plateauing 'shark-fin' shaped curve that is often seen in experimental supercapacitor characterisation. The resulting curve still presents a relatively curved shape and as such poses the same problem as before, in that the determination of where to take the gradient for the characteristic capacitance is undefined. In order to address this, further evaluations of varying parallel capacitances are investigated.

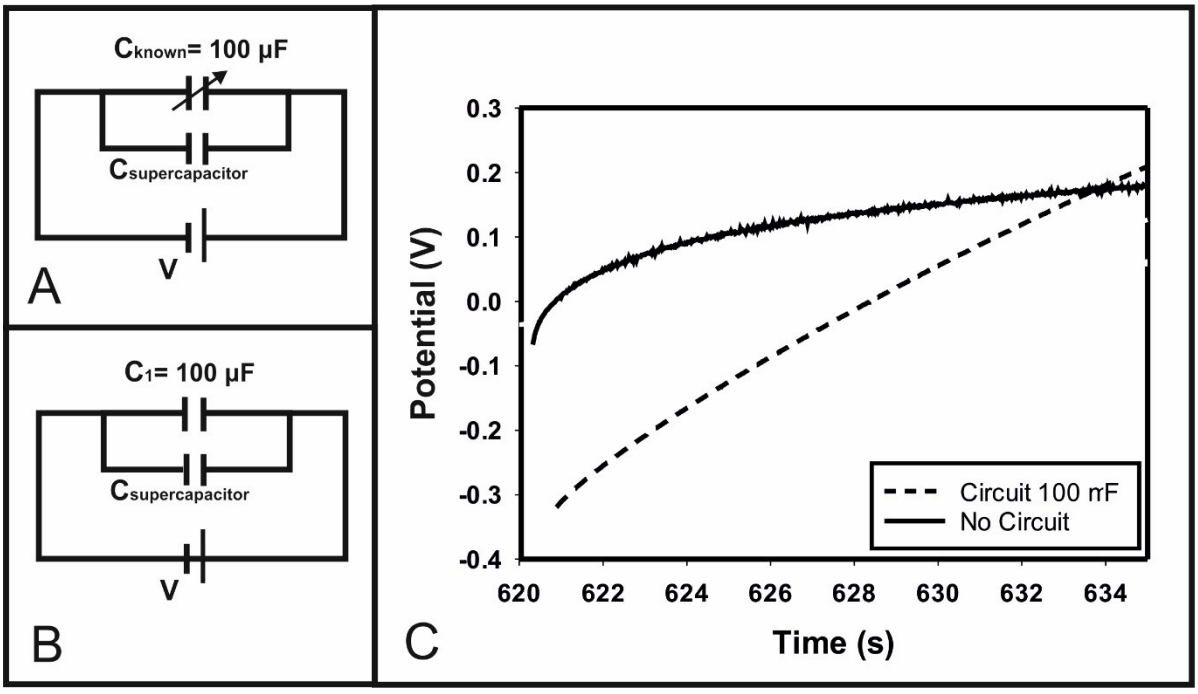
By increasing the parallel capacitance, the effect on the nominal gradient of the charging cycles can be seen. ESI Figure 3 shows the arrangements for measuring in parallel with a 200 μF capacitor, or two 100 μF capacitors, which as shown previously are the same. In this case, the line is significantly smoother still and straighter. Increasing the parallel capacitance further still, to 620 μF, shown in ESI Figure 4, the charge cycles are near linear in behaviour. As a result, the gradient of the whole line can be utilised to determine the capacitive properties of the system, and equation 5 from the main body of text can be used to interpret the capacitance for the working electrode.

The result of this analysis is a systematic approach for providing a true value of the capacitance of an electrode without the risk of misinterpretation of the data. Also by utilising the component in a system the approach to the analysis of electrode properties, the set-up is limited to a 2-wire analysis, which is commercially more useful in terms of supercapacitors. This is a benefit, also, as there is yet to be a standardized approach to such analysis, as shown in Table 1. This develops a uniform approach for all researchers, providing a system that improves repeatability and cohesion amongst the field. The approach consists of the following steps;

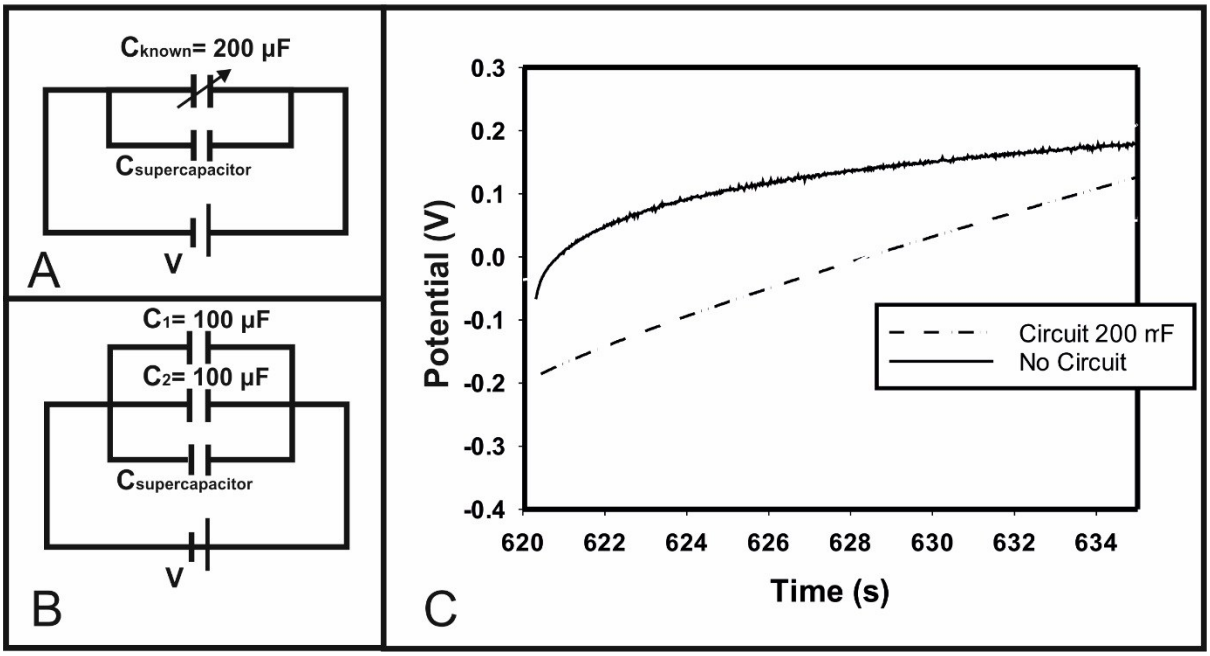
1) Perform charge/discharge cycles with the system alone, without any parallel capacitance;
2) Interpret the capacitance without the circuit;
3) Insert the variable capacitor/capacitor circuit in parallel with a low capacitance, of the order of the value extracted from the interpretation without the circuit in steps 1) and 2);
4) Re-interpret the capacitance from the resulting charge cycle, with the parallel circuit in place.
5) If the charge properties are still not linear increase the capacitance until a linear signal is achieved;
6) Interpret the true capacitance from the resulting linear charge response.



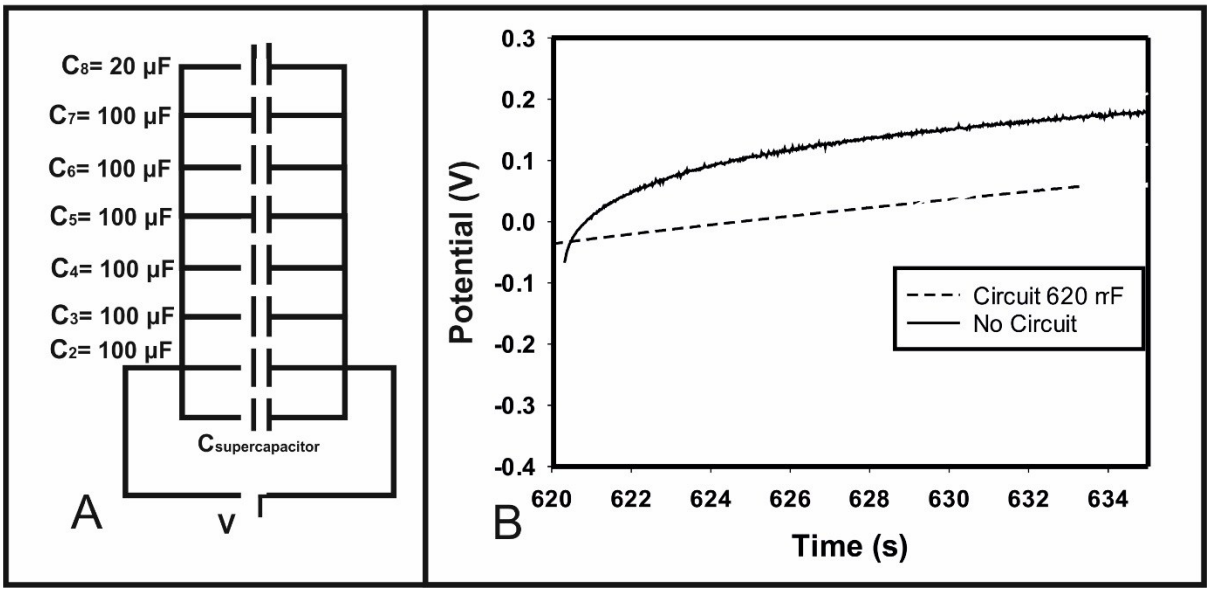
ESI Figure 1 Capacitance circuits for the three-capacitor system, A) in parallel and B) in series.



ESI Figure 2 Evaluation of the capacitance of the supercapacitor integrated into a parallel circuit for 100 µF.



ESI Figure 3 Evaluation of the capacitance of the supercapacitor integrated into a parallel circuit for 200 µF.



ESI Figure 4 Evaluation of the capacitance of the supercapacitor integrated into a parallel circuit for 620 µF.