



## Interlaboratory study assessing the analysis of supercapacitor electrochemistry data

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### HIGHLIGHTS

- Supercapacitor electrochemistry data analysed by 14 different laboratories.
- Constant current tests gave lower variability in capacitance than CV tests.
- Large variation in capacitance results obtained for ‘non-ideal’ devices.
- Capacity should be reported for reliable comparison of device performance.
- Researchers must be clear on their definition of ‘specific capacitance’.

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## ABSTRACT

Supercapacitors are fast-charging energy storage devices of great importance for developing robust and climate-friendly energy infrastructures for the future. Research in this field has seen rapid growth in recent years, therefore consistent reporting practices must be implemented to enable reliable comparison of device performance. Although several studies have highlighted the best practices for analysing and reporting data from such energy storage devices, there is yet to be an empirical study investigating whether researchers in the field are correctly implementing these recommendations, and which assesses the variation in reporting between different laboratories. Here we address this deficit by carrying out the first interlaboratory study of the analysis of supercapacitor electrochemistry data. We find that the use of incorrect formulae and researchers having different interpretations of key terminologies are major causes of variability in data reporting. Furthermore we highlight the more significant variation in reported results for electrochemical profiles showing non-ideal capacitive behaviour. From the insights gained through this study, we make additional recommendations to the community to help ensure consistent reporting of performance metrics moving forward.

## 1. Introduction

In recent years, interest has risen in fast-charging energy storage devices such as supercapacitors, driven by the current climate and energy crises [1–6]. In the past three years alone, more than 20,000 publications have been published in this area [7], and various approaches have been taken to attempt to improve the energy and power performances of supercapacitors. The performances of existing carbon electrode materials have been improved through heteroatom doping, compositing with pseudocapacitive materials, and by structure optimisation [8–10]. Novel electrode materials with performances on-par with or exceeding carbon materials have also been developed, including MXenes, metal-organic frameworks (MOFs), and transition metal oxides (TMOs) [11–13]. Further research has focussed on developing new electrolytes with higher stable voltage windows and greater ionic conductivities [14–16]. While improving the performance of these devices is crucial, successfully integrating supercapacitors with other energy conversion and storage technologies, including in practical and wearable devices, is also critical for many future applications [17,18]. In all these papers, performance metrics such as total capacitance, specific capacitance, and internal resistance are commonly reported by researchers [19–24]. However, with more groups beginning to venture into the field and an increasing number of reported devices exhibiting non-ideal capacitive behaviour, variation in data analysis can lead to inconsistent and unreliable results being reported across different laboratories.

It is crucial to have consistent reporting of performance data between different researchers in this field. Many reports have emerged over the past decade discussing the best practices for data analysis and data reporting for energy storage devices [25–38]. These studies have primarily focused on reporting the correct formulae and methods for data analysis. However, there is yet to be an empirical study investigating whether researchers in the field are correctly implementing these recommendations, and assessing the variation in data analysis and reporting between different laboratories. Here, we address this issue by conducting the first interlaboratory study to assess the variation in reporting of performance metrics from galvanostatic charge-discharge (GCD) and cyclic voltammetry (CV) datasets for lab-scale fast-charging supercapacitor devices, including devices that display both ideal and non-ideal capacitive behaviour. This study does not address variation in experimental supercapacitor assembly, but only the data analysis of pre-supplied data sets. From this study, we conclude that, while most groups obtained similar results despite differences in analysis methods, misuse of formulae could lead to incorrect values being reported. Furthermore, different interpretations of terminology between laboratories can result in different values being reported for a given performance metric, potentially confusing researchers who are new to the field. In addition, the variation in results is significantly amplified if the device shows non-ideal capacitive behaviour, highlighting that calculating capacitance for such systems is more challenging than for devices

displaying more ideal capacitive behaviour. From these insights, we reinforce correct analysis procedures and make several further recommendations to ensure consistent analysis and reporting of performance metrics across researchers. This should significantly benefit the field in the future.

## 2. Methods

## 2.1. Experimental

All experimental work was carried out by J.W.G. at the University of Cambridge, one of the study coordinators. Five lab-scale symmetric two-electrode supercapacitor devices, Cells 1–5, were prepared using the below methods.

## 2.1.1. Materials

Materials were purchased from Sigma Aldrich (Merck) unless specified below. All materials were used without additional modification unless specified below.

Four different electrode materials were used in this study; (i) YP-50F activated carbon, (ii) YP-80F activated carbon, (iii) ammonia-modulated  $\text{Cu}_3(\text{HHTP})_2$  (HHTP = 2,3,6,7,10,11-hexahydroxy-triphenylene), and (iv) DMF-modulated  $\text{Cu}_3(\text{HHTP})_2$  (DMF = dimethylformamide). YP-50F and YP-80F were purchased from Kuraray. Ammonia and DMF-modulated  $\text{Cu}_3(\text{HHTP})_2$  were synthesised using existing literature methods [39].  $\text{Cu}_3(\text{HHTP})_2$  is a porous, layered, electrically conductive metal-organic framework (MOF).

Three different electrolytes were used in this study; (i) 1 M tetraethylammonium tetrafluoroborate ( $\text{NEt}_4\text{BF}_4$ ) in acetonitrile, (ii) 1 M tetraethylphosphonium tetrafluoroborate ( $\text{PEt}_4\text{BF}_4$ ) in acetonitrile, and (iii) undiluted 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (BMIM-TFSI) ionic liquid.  $\text{PEt}_4\text{BF}_4$  was purchased from TCI Chemicals. BMIM-TFSI was purchased from IoLiTec Ionic Liquids Technologies.  $\text{NEt}_4\text{BF}_4$  and  $\text{PEt}_4\text{BF}_4$  were dried under vacuum at 100 °C for 72 h before being transferred to a  $\text{N}_2$  glovebox. Anhydrous acetonitrile (ACN) was purged with  $\text{N}_2$  for 3 h before being taken into a glovebox, where it was further dried using activated 3 Å molecular sieves. BMIM-TFSI was dried at room temperature under a dynamic vacuum for 120 h before being transferred to a  $\text{N}_2$  glovebox.

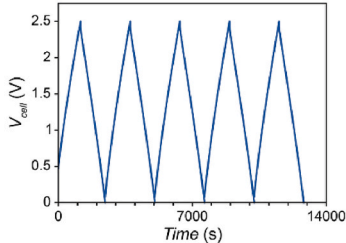
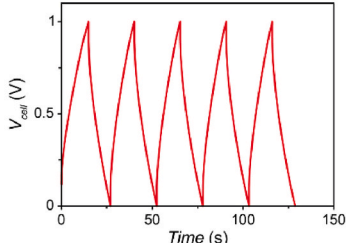
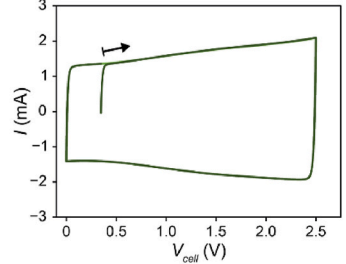
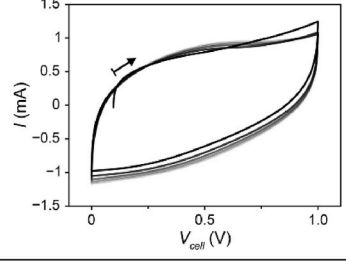
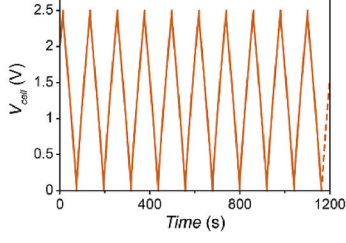
Participating groups did not have any information about the electrode materials and electrolytes used to assemble the supercapacitors when performing the analysis.

## 2.1.2. Electrode film preparation

Using an established literature method, freestanding composite electrode films were prepared [40]. The electroactive material(s) were mixed with ethanol (approx. 1.5 mL) and the mixture was sonicated for 5 min to create a loose slurry. This slurry was combined with polytetrafluoroethylene (PTFE) dispersion (60 wt% in water) in a few drops

of ethanol. The mixture was manually stirred under ambient conditions until a film was formed. To ensure homogeneity, the film was kneaded for 20 min and then rolled into a freestanding electrode film using a homemade aluminium rolling pin. The film was then dried under vacuum at 75–100 °C for a minimum of 48 h to remove any remaining ethanol. To guarantee high rate performance, acetylene black (Thermo Fisher Scientific; measured BET area = 62 m<sup>2</sup> g<sup>-1</sup>) was added to films

made with ammonia- and DMF-modulated Cu<sub>3</sub>(HHTP)<sub>2</sub>. In these films, the masses of components were calculated so that the final films had a composition of 85 wt% Cu<sub>3</sub>(HHTP)<sub>2</sub>, 10 wt% acetylene black, and 5 wt% PTFE. Films made with YP-50F and YP-80F activated carbons did not require any added conductive additive, and therefore had a final composition of 95 wt% activated carbon and 5 wt% PTFE. All films were of uniform thickness, measuring between 250 and 270 µm.

| File Number           | Graphical Representation  | Cell Parameters                  | Characterisation Parameters  | Analysis Requested   |
|-----------------------|---|----------------------------------|--|--|
| <b>1</b><br>Ideal     |    | $m_1 = 3.3$ mg<br>$m_2 = 3.1$ mg | GCD<br>$I = 0.326$ mA<br>0 – 2.5 V<br>5 cycles                         | Total Capacitance, $C_T$ (F)<br>Specific capacitance of electrode material, $C_g$ (F g <sup>-1</sup> )<br>Total internal resistance, $R$ (Ω) |
| <b>2</b><br>Non-ideal |   | $m_1 = 1.9$ mg<br>$m_2 = 2.0$ mg | GCD<br>$I = 2.85$ mA<br>0 – 1 V<br>5 cycles                            | Total Capacitance, $C_T$ (F)<br>Specific capacitance of electrode material, $C_g$ (F g <sup>-1</sup> )<br>Total internal resistance, $R$ (Ω) |
| <b>3</b><br>Ideal     |  | $m_1 = 3.1$ mg<br>$m_2 = 3.2$ mg | CV<br>$\nu = 10$ mV s <sup>-1</sup><br>0 – 2.5 V<br>5 cycles           | Total Capacitance, $C_T$ (F)<br>Specific capacitance of electrode material, $C_g$ (F g <sup>-1</sup> )                                       |
| <b>4</b><br>Non-ideal |  | $m_1 = 2.9$ mg<br>$m_2 = 3.1$ mg | CV<br>$\nu = 10$ mV s <sup>-1</sup><br>0 – 1 V<br>5 cycles             | Total Capacitance, $C_T$ (F)<br>Specific capacitance of electrode material, $C_g$ (F g <sup>-1</sup> )                                       |
| <b>5</b><br>Ideal     |  | $m_1 = 6.1$ mg<br>$m_2 = 6.6$ mg | GCD<br>$I = 12.6$ mA<br>0 – 2.5 V<br>10000 cycles<br>(10 cycles shown) | Capacitance retention after 10000 cycles (%)   |

**Fig. 1.** Summary of the data files sent to each of the participating groups, including a graphical depiction of the dataset, key cell parameters, characterisation parameters, and the requested analysis.  $m_1$  and  $m_2$  (mg) are the masses of the two electrodes in each cell.  $\nu$  (mV s<sup>-1</sup>) is the scan rate used in CV experiments.  $I$  (mA) is the constant charge and discharge current used in GCD experiments.

### 2.1.3. Supercapacitor assembly

Coin cells were assembled in Cambridge Energy Solutions CR2032 SS316 coin cell cases. All cells were two-electrode cells and did not utilise a third reference electrode. Electrodes were cut from freestanding composite films using either  $\frac{3}{16}$ ,  $\frac{1}{4}$ , or  $\frac{3}{8}$  inch electrode cutters, and had areal mass loadings of between 9 and 11 mg cm<sup>-2</sup>. The cells were assembled in a N<sub>2</sub> glovebox (O<sub>2</sub> < 0.1 ppm; H<sub>2</sub>O < 0.1 ppm).

Cell 1 was assembled with YP-50F electrodes (3.3 mg, 3.1 mg, 0.317 cm<sup>2</sup>) and undiluted BMIM-TFSI electrolyte. Cell 2 was assembled with ammonia-modulated Cu<sub>3</sub>(HHTP)<sub>2</sub> electrodes (1.9 mg, 2.0 mg, 0.178 cm<sup>2</sup>) and 1 M PEt<sub>4</sub>BF<sub>4</sub> in ACN electrolyte. Cell 3 was assembled with YP-80F electrodes (3.2 mg, 3.1 mg, 0.317 cm<sup>2</sup>) and 1 M NEt<sub>4</sub>BF<sub>4</sub> in ACN electrolyte. Cell 4 was assembled with DMF-modulated Cu<sub>3</sub>(HHTP)<sub>2</sub> electrodes (2.9 mg, 3.1 mg, 0.317 cm<sup>2</sup>) and 1 M NEt<sub>4</sub>BF<sub>4</sub> in ACN electrolyte. Finally, Cell 5 was assembled with YP-50F electrodes (6.1 mg, 6.6 mg, 0.713 cm<sup>2</sup>) and 1 M NEt<sub>4</sub>BF<sub>4</sub> in ACN electrolyte. The volume of electrolyte added was kept consistent between cells (approximately 10 drops from a Pasteur pipette). Whatman glass microfiber filters (GF/A) were used as separators, and were dried under vacuum at 100 °C for 24 h before use. Each coin cell contained two stainless steel spacer disks and one stainless steel conical spring to ensure adequate pressure in the cells. The coin cells were hermetically sealed at 80 kg cm<sup>-2</sup> for 1 min before being removed for testing.

### 2.1.4. Electrochemical measurements

All electrochemical measurements were carried out under ambient conditions at the University of Cambridge using a BioLogic BCS-800 Series ultra-precision battery cyler and a Biologic VSP-3e potentiostat. Each cell was used to generate one dataset for analysis, producing the corresponding datasets File 1–5. A summary of each dataset, along with cell assembly parameters, is provided in Fig. 1.

Galvanostatic charge-discharge (GCD) experiments were conducted on Cells 1 and 2. Variation in the magnitude of the applied constant current during the GCD experiments was negligible. Cyclic voltammetry (CV) experiments were carried out on Cells 3 and 4. A long-term cycling GCD experiment was carried out on Cell 5. The electrochemical measurements carried out on each cell are also summarised in Fig. 1.

## 2.2. Interlaboratory study details

14 research groups participated in the analysis study out of a total of 38 groups who were invited. Web of Science was used to find appropriate research groups to invite. Groups were selected to be invited if they had published research containing the keyword “supercapacitors” within the past 3 years. No judgement was made on the quality of a group’s publications when inviting them to the study. Groups from a range of different countries were invited to attempt to ensure the diversity of the study. The role of the participating groups was to analyse the electrochemistry data provided by the coordinating group independently. Experimental work was carried out for the sole purpose of obtaining standardised datasets for the participating groups to analyse. The coordinating group (Y.C., J.W.G., D.L., and A.C.F. at the University of Cambridge) did not provide analysis of the electrochemistry data for this study. Each participating group was provided with identical data files and instructions, specifically the five datasets (File 1–5) as .txt files, and an instruction sheet detailing the required analysis. A copy of the data files and the instruction sheet is provided as Supplementary Data. Researchers can check if they are performing the analysis of supercapacitor data correctly by analysing the data files provided and comparing their results to those given for each data file in the Results and Discussion section below, and in SI Section 4.

Participating groups submitted their analysis results to the coordinating group. The coordinating group then performed meta-analyses of the provided results. See the Supplementary Information for information on how the results provided were processed (SI Section 1).

The participants were asked to calculate a range of electrochemical parameters from the provided datasets including total capacitance (F), specific capacitance (F g<sup>-1</sup>), and total internal resistance (Ω). The analysis requested from each dataset is summarised in Fig. 1. All results received have been anonymised and randomised. A full list of the reported results is shown in the Supplementary Information (SI Section 4). It is important to note that not all participating groups supplied data for each data file. For Files 1–4, only data from cycle 3 is presented in the Results and Discussion section for simplicity. All cycles showed the same trends.

## 3. Results and discussion

The scope of this interlaboratory study was limited to assessing consistency in the analysis and reporting of supercapacitor electrochemistry data. To achieve this, five electrochemistry datasets (Fig. 1) were sent to each participating group along with instructions for the analysis to be performed on each file. Following the independent analysis by the 14 participating groups, the coordinating group performed a meta-analysis of the combined results.

The study also aimed to assess differences in the analysis and reporting of data from cells displaying both “ideal” and “non-ideal” capacitive performances. Therefore, Files 1 and 3 were from ideal supercapacitor cells, which display approximately linear triangular GCD and rectangular CV profiles, indicating charge storage is dominated by electric-double layer contributions. In contrast, Files 2 and 4 were collected from non-ideal supercapacitor cells, which display non-linear quasi-triangular GCD and quasi-rectangular CV profiles, indicating that either other charge storage mechanisms (e.g. fast redox reactions) contribute to the charge stored, or that the device has a high resistance. The classification of each dataset as ideal or non-ideal is indicated in Fig. 1.

### 3.1. Galvanostatic charge-discharge (GCD) analysis

#### 3.1.1. Total capacitance

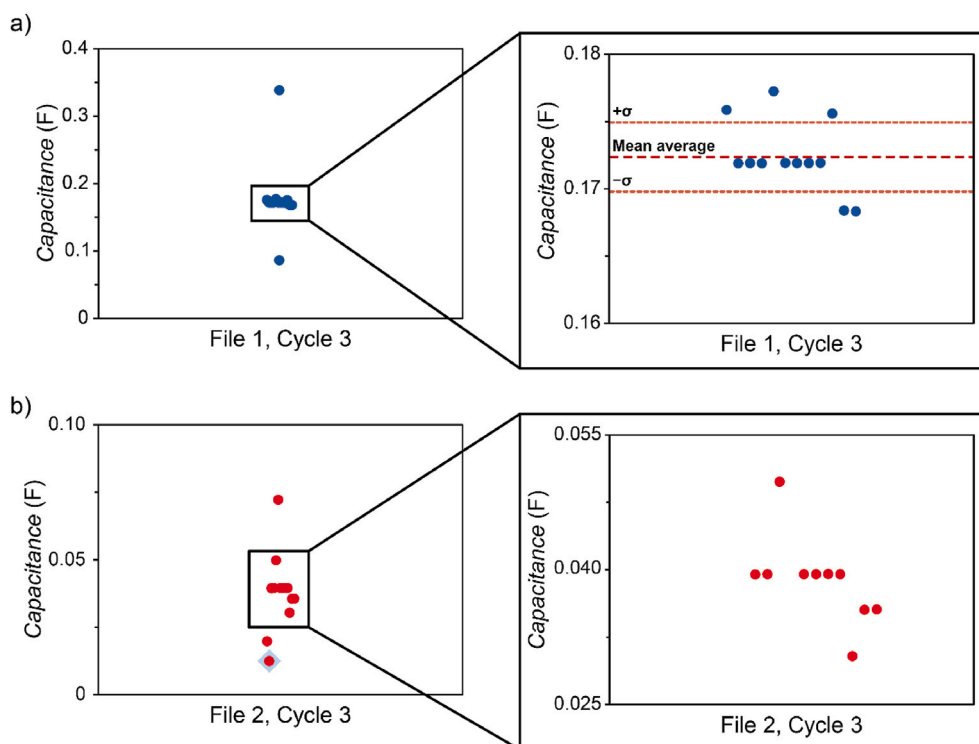
File 1 is from an ideal supercapacitor and displays a linear GCD profile, as expected for a device where the charge is solely stored by non-Faradaic ion adsorption in the electric double-layer. As shown in Fig. 2a, most participating groups obtained comparable results when calculating the total capacitance from File 1, with over 50% of participants lying within one sigma of the adjusted mean average. This is despite differences in analysis methods such as the formulae used and differences in determining the discharge slope. See the Supplementary Information for detailed information on the analysis methods used by each participating group. However, extreme anomalies were observed, accounting for approximately 14% of reported results. These anomalies were due to incorrect formulae used to calculate the total capacitance, with the results being either too small or too large by a factor of two (SI Section 3).

Despite the small size of this study, this striking result reinforces the need to remind the community of the correct formula for calculating total capacitance from linear ideal GCD datasets displaying double-layer charge storage to eliminate any potential anomalies in the literature. Having an agreed and established analysis protocol that is accessible to all would help to ensure consistent and replicable results can be generated. The correct general formula for total capacitance,  $C_T$ , is shown in Equation (1) [28,30]:

$$C_T = \frac{I}{\left(\frac{\Delta V}{\Delta t}\right)} \quad (1)$$

where  $I$  is the constant charging/discharging current (A), and  $\frac{\Delta V}{\Delta t}$  is the gradient of the discharge slope (V s<sup>-1</sup>).  $C_T$  has units of Farads (F). This equation assumes that the gradient is constant over the chosen voltage range of analysis. While most groups used Equation (1), Group 12 analysed the dataset using a different approach also seen in the literature





**Fig. 2.** Total capacitance (F) as reported by participating groups for (a) File 1, from an ideal supercapacitor, and (b) File 2, from a non-ideal supercapacitor. Plots on the left show all data points reported and plots on the right show a zoomed-in view of the enclosed section, highlighting the data distribution about the adjusted mean average where appropriate. This is the mean average obtained after omitting anomalous values that were calculated using incorrect methods. For File 1, anomalous values are excluded from the enclosed section of the plot.  $\sigma$  is the standard deviation in the adjusted mean values. The adjusted mean value for File 1 is 0.172 F. No adjusted mean average value was calculated for File 2 as the use of different equations during the analysis of this file makes the criteria for classification of an anomaly unclear. The highlighted data point in the results of File 2 (blue) is the total capacitance reported by Group 3. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

[27,30,41]. This method involves calculating the energy stored in the device by integration of the discharge curve and using this value to calculate the capacitance via the energy-capacitance relationship for an ideal supercapacitor (SI Section 3). This approach gives comparable results to Equation (1) for ideal double-layer datasets. All groups analysed the discharge profile to calculate the capacitance. We recommend that research groups report the voltage range used to calculate the discharge slope as this can impact the final results. Groups should also report whether the Ohmic voltage drop was excluded from the calculation of the discharge slope.

In contrast to File 1, File 2 is from a non-ideal supercapacitor which does not display a linear GCD profile, with the discharge slope varying with voltage (Fig. 1; File 2). 11 out of 14 groups analysed this dataset using Equation (1). This gave a larger variation in results compared to File 1 as the non-linear shape of the GCD amplified differences in analysis, including the voltage range used to determine the discharge slope and whether the Ohmic voltage drop was excluded from the calculation (Fig. 2b). As with File 1, two groups used incorrect equations to calculate the total capacitance. To attempt to account for the non-linearity of the data, Groups 3 and 12 used approaches which correspond to calculating the discharge energy via integration, and then calculating the capacitance from this (SI Section 3). While Group 12 converted the calculated discharge energy into a capacitance by equating to the energy stored in an ideal supercapacitor, the same approach they used for File 1, Group 3 equated to the energy stored in an ideal battery due to the non-linear nature of the discharge curve. This resulted in a lower reported capacitance value of 0.012 F (highlighted in Fig. 2b in blue; SI Section 3).

Ultimately, if capacitance is a function of voltage as for File 2, all of these methods only give a single average capacitance value which does not accurately reflect the complete behaviour of the cell. This may lead to inflated capacitance values and overreporting of the performance of

non-ideal devices. If Equation (1) is used to calculate capacitance for a non-ideal device, researchers should only calculate this over the voltage range where the capacitance is constant, and should clearly report this voltage range alongside the capacitance. It must be noted that several groups raised concerns about analysing the non-ideal profile of File 2 using ideal capacitive methods. It was suggested by three groups that, rather than capacitance, capacity is a more suitable electrochemical property for non-ideal devices due to the variation of capacitance with cell voltage [42–44]. Indeed, the use of capacity, would be expected to give identical results for different researchers, and would remove the ambiguity and confusion seen in Fig. 2b. Furthermore, capacity can be calculated for all energy storage devices displaying a wide range of GCD curves, and thus is an appropriate performance metric to compare the performances of many energy storage devices, some of which may have unclear charge storage mechanisms. Therefore, we recommend calculating and reporting capacity for all supercapacitors, especially those displaying non-linear discharge curves. This is crucial for ensuring reliable reporting of performance from non-ideal devices. Capacity can be calculated using Equation (2) below:

$$\text{Capacity} = I \bullet \Delta t \quad (2)$$

where  $I$  is the discharge current (A), and  $\Delta t$  is the discharge time (s). This equation gives capacity in Coulombs (C), although it is often converted to have units of mAh. The discharge energy, calculated via integration, is also a reliable performance metric to indicate the performance of all energy storage devices [27,41]. We recommend that this is also reported for all supercapacitors. Furthermore, this integral approach should be used to calculate the energy and power of non-ideal devices, and is also applicable for ideal devices (SI Section 3). Both energy density and power density should only be calculated and reported for two-electrode devices.

A previous report on the analysis of supercapacitor data suggested a

different equation for the analysis of non-ideal devices (SI Section 3) [26]. However, we do not believe that this method is correct as it gives a capacitance value of 0.385 F for File 2, significantly higher than the other methods discussed above. We discourage the use of this equation in the future.

### 3.1.2. Specific capacitance

As shown in Fig. 3, most of the reported specific capacitance values for both File 1 and File 2 could be split into two distinct groups. In both cases, 54–57% of values fall into the lower group, and 36–37% of values fall in the upper group, with the values in the upper group being approximately four times larger than those in the lower group. Please note that most participating groups reported values in the same specific capacitance group for both Files 1 and 2 apart from 2 participating groups. There is a greater spread in the reported specific capacitance values in both the upper and lower groups for the non-ideal dataset File 2, reflecting the larger variation in the reported total capacitance discussed above.

The main reason behind this distinctive difference was how different researchers interpreted the term “specific capacitance”. For participants reporting values within the lower group, specific capacitance was interpreted as the specific capacitance of the full cell (i.e. the specific capacitance of the total mass of active electrode material in the two-electrode cell assembly) [28]. The general formula used in this case is given in Equation (3):

$$C_{g,1} = \frac{C_T}{M_{cell}} \quad (3)$$

where  $C_T$  (F) is the total capacitance as calculated in the previous section and  $M_{cell}$  (g) is the total mass of the two electrodes in the cell (i.e.,  $M_{cell} = m_{e,1} + m_{e,2}$ ; where  $m_{e,1}$  and  $m_{e,2}$  are the masses of the two electrodes, respectively).  $C_{g,1}$  has units of  $F g^{-1}$ . This equation normalises the cell capacitance by the total mass of the two electrodes in the cell. In this study, only the masses of the electrodes in each cell were provided to participating groups. One group recommended that specific capacitance be calculated using the total mass of the overall cell including the separators, current collectors, casings, and other components.

For participants within the upper group, specific capacitance was interpreted as the specific capacitance of the active electrode material in a single electrode (i.e., independent of device architecture) [25,28,38]. The general formula used in this case is given by Equation (4):

$$C_{g,2} = \frac{2C_T}{m_{ave}} \quad (4)$$

where  $m_{ave}$  is the average mass of one electrode in the cell ( $m_{ave} = \frac{1}{2}(m_{e,1} + m_{e,2})$ ).  $C_{g,1}$  has units of  $F g^{-1}$ . This interpretation results in a specific capacitance value four times greater than the previous interpretation. However, it must be noted that Equation (4) assumes that the

capacitances of the positive and negative electrodes are equal. Although this may not be the case in practice, the value obtained from Equation (4) will still give an indication of the performance of a device and is often quoted in literature, as seen from the fact that 36–37% of the groups in this study reported  $C_{g,2}$ . We recommend that three-electrode measurements are also performed to independently evaluate the capacitance of both the positive and negative electrode independently in their respective operating potential windows. Derivations for Equations (3) and (4) are stated in the Supplementary Information (SI Section 2).

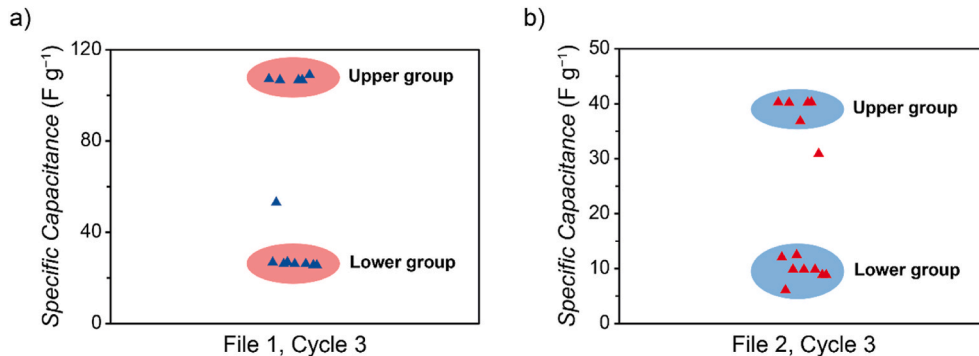
This result demonstrates that different interpretations of specific capacitance exist within the community, and these can lead to significantly different reported values for the same performance metric. This stresses the need for clearer definitions when reporting specific capacitance to eliminate ambiguity in reported results. Therefore, we recommend clearly defining how “specific capacitance” is interpreted when reporting values for this performance parameter in the literature. It is crucial to indicate if the reported specific capacitance values refer to the electrode material in a two-electrode cell, to the electrode material independent of device architecture (i.e., a “pseudo” single electrode measurement), or to the overall device including non-active components such as current collectors. This would prevent confusion within the literature and allow for a more straightforward comparison of results. The use of three-electrode measurements is also recommended to determine the capacitance of a single electrode. This would remove confusion on the terminology for two-electrode devices.

### 3.1.3. Internal resistance

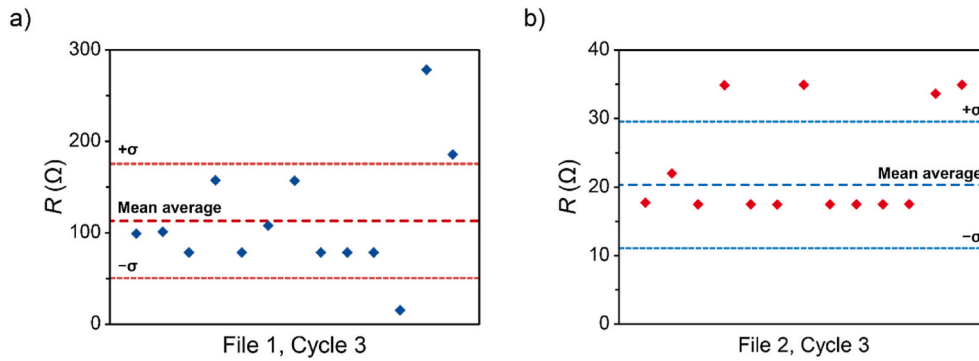
As shown in Fig. 4, reported total internal resistance values from both Files 1 and 2 can be divided into two groups, independent of whether the dataset is classified as ideal or non-ideal. This division is the result of several groups using the incorrect formula, where the Ohmic voltage drop at the start of discharging is divided by the current applied during the GCD experiment. Instead, the change in current when transitioning from charging to discharging,  $\Delta I$ , needs to be used for this calculation. Assuming the magnitude of the charge and discharge currents is equal and that no potentiostatic or rest step is applied between charge and discharge, as is the case for these datasets, the current is changing from  $+I$  to  $-I$  during this transition. Therefore,  $\Delta I$  is equal to  $2I$ , and the voltage drop should be divided by this value to accurately calculate the total internal resistance, as in Equation (5) [28,31,45]:

$$R = \frac{\Delta V_{drop}}{2I} \quad (5)$$

where  $R$  is the total internal resistance ( $\Omega$ ),  $\Delta V_{drop}$  is the Ohmic voltage drop (V), and  $I$  is the charging/discharging current applied (A). Please note that  $\Delta V_{drop}$ , the Ohmic voltage drop, is distinct from  $\Delta V$ , the change in voltage during discharge, given in Equation (1). This result demonstrates the need to reinforce correct analysis procedures set out in



**Fig. 3.** Specific capacitance results ( $F g^{-1}$ ) as reported by participating laboratories for (a) File 1 (ideal), and (b) File 2 (non-ideal). Two distinct groups of values are seen in both plots (highlighted). The mean value for the upper group in File 1 is  $108.0 F g^{-1}$ . The mean value for the lower group in File 1 is  $26.9 F g^{-1}$ . The mean value for the upper group in File 2 is  $39.8 F g^{-1}$ . The adjusted mean value for the lower group in File 2 is  $10.5 F g^{-1}$ .



**Fig. 4.** Total internal resistance ( $R$ ,  $\Omega$ ) as reported by participating groups for (a) File 1 (ideal), and (b) File 2 (non-ideal), highlighting the mean average and an interval of one standard deviation,  $\sigma$ , either side of this value. Using Equation (5), total internal resistance values of approx. 78.6  $\Omega$  and 17.5  $\Omega$  are obtained for Files 1 and 2, respectively.

previous studies as they are not being strictly followed by the community [31,34]. Incorrect calculation of the total internal resistance will also lead to inaccurate reporting of the power,  $P$ , of a device (in Watts; W), which can be expressed as shown in Equation (6) for an ideal supercapacitor [31,33]:

$$P = \frac{V_{cell}^2}{4R} \quad (6)$$

This equation is only valid for ideal supercapacitors which display linear GCD plots. See the SI for details on calculating the power of a non-ideal device (SI Section 2).

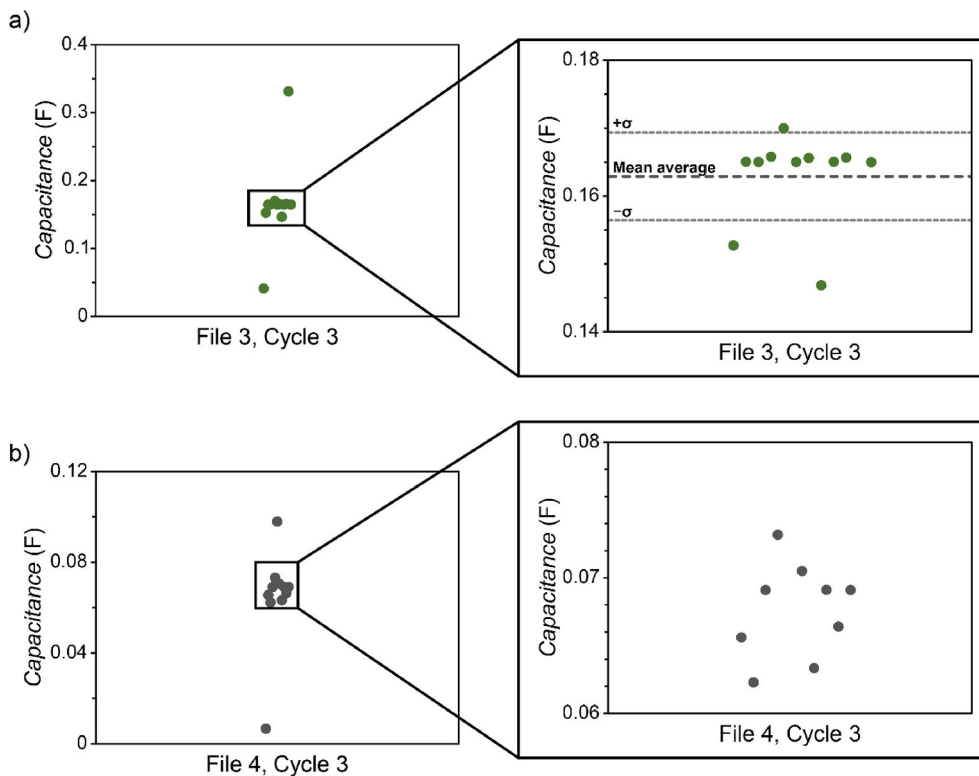
Further variation within each of the two groups of values is a result of differences in determining the voltage drop from the GCD data. Assigning the voltage drop is highly subjective and varies from researcher to researcher. To eliminate this variation going forwards, we

recommend the agreement and application of a consistent criterion for measuring the voltage drop from GCD cycles, as outlined in previous work [31,45]. For this study, the internal resistance was calculated at a single, fixed applied current. Measuring the voltage drop across a series of GCD experiments with different applied currents would give a more reliable resistance calculation.

### 3.2. Cyclic voltammetry (CV) analysis

#### 3.2.1. Total capacitance

The reported total capacitance values from CV data, shown in Fig. 5, show a similar pattern to those calculated from GCD data shown in Fig. 2. As discussed in Section 1.1, extreme anomalies were observed for both Files 3 and 4, accounting for approximately 14–20% of reported results. These were due to the use of incorrect formulae during analysis.



**Fig. 5.** Total capacitance results (F) collected from participating groups for (a) File 3 from an ideal supercapacitor, and (b) File 4 from a non-ideal device. Plots on the left show all data points reported and plots on the right show the zoomed-in views of the enclosed section, highlighting the adjusted mean average and an interval of one standard deviation,  $\sigma$ , on either side of this value where appropriate. The adjusted mean for File 3 is 0.163 F. No adjusted mean average value is provided for File 4 due to ambiguity over whether capacitance should be calculated for this file.

This highlights the need to remind the community of the correct formula for calculating total capacitance from CV data to eliminate anomalies in the literature. The correct formula for calculating total capacitance from CV data for ideal supercapacitors is given in Equation (7):

$$C_T = \frac{\int_{V_1}^{V_2} I dV}{(V_2 - V_1) \bullet v} \quad (7)$$

where  $(V_2 - V_1)$  is the voltage window, and  $V_2$  and  $V_1$  are the bounds of the discharge voltage window where capacitive behaviour is observed (V),  $v$  is the scan rate ( $V s^{-1}$ ),  $I$  is the discharge current (A), and  $dV$  is the infinitesimal change in cell voltage (V) [28,30]. In this study, 6 of the 14 participating groups integrated across the entire CV curve (i.e., charge and discharge) when calculating total capacitance. This requires dividing by an additional factor of two compared to Equation (7) above to account for this. However, in future, we recommend that all researchers use the discharge area only (i.e., negative current voltammetric region) when calculating total capacitance from CV data as this avoids including contributions from any irreversible Faradaic reactions that may occur during charging.

Similar to the GCD data discussed in Section 1.1, the CV datasets consisted of one from an almost ideal supercapacitor (File 3), which displayed a rectangular CV profile, and another from a non-ideal device (File 4), which displayed a quasi-rectangular CV profile. As with the non-ideal GCD dataset (File 2), several groups raised concerns regarding calculating capacitance for File 4. As noted previously, capacity may be a more suitable electrochemical property for non-ideal devices. This echoes previous reports on best practices, and the non-ideal behaviour resulted in a more significant variation in results when calculating capacitance for File 4 than File 3 [42–44].

This work also finds that the spread of reported total capacitance values calculated from CV datasets is greater than that from GCD datasets. This can be seen by comparing the standard deviations for the reported total capacitance values from File 1 (1.5%) and File 3 (4.0%), a GCD and CV dataset from an ideal device, respectively. This shows that calculating performance metrics from GCD datasets is more reliable than from CV datasets. This is primarily due to the large variation in methods for integrating the discharge curve of the CV. This study, therefore, recommends that researchers use GCD datasets to calculate performance metrics instead of CV datasets where possible. CV data should primarily be used to qualitatively assess the charge storage mechanism of the supercapacitor.

### 3.2.2. Specific capacitance

Unlike the specific capacitance results reported from GCD datasets (Section 1.2), the specific capacitance results from CV datasets can be divided into 3 distinct groups based on three different formulae used

(Fig. 6). For the upper group, the specific capacitance was calculated using Equation (4), stated above as  $C_{g,2}$ . For the middle group, the specific capacitance was calculated using an incorrect formula that differs from Equation (4) with the factor of two on the numerator missing. For the lower group, specific capacitance was calculated using Equation (3), stated above as  $C_{g,1}$ .

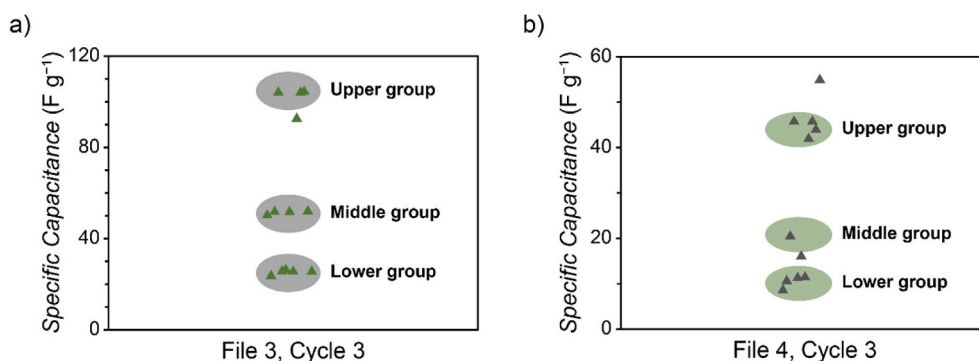
The greater variety of formulae used to calculate specific capacitance for CV datasets compared to GCD datasets was due to additional confusion when using the area of the entire CV cycle during the analysis, resulting in the use of an incorrect formula for calculating the specific capacitance from CV data. Overall, this data reinforces several points stated previously. Firstly, one needs to clearly define what “specific capacitance” means when reporting values for this metric to avoid confusion. Secondly, the community needs to be reminded of the correct formula for calculating specific capacitance from CV data, as 29% of participants used an incorrect formula in this study. The three groups of specific capacitance values are less visible for File 4 as fewer participants reported values for this dataset due to its non-ideal behaviour. This further illustrates that it may be more suitable to characterise energy storage devices with non-ideal charge storage mechanisms with other, more appropriate performance metrics.

A minor source of variation in the capacitance values calculated from CV data was whether a manual or computational method was being used to calculate the CV integral. The computational integration calculation is often more accurate than manual analysis, where approximations to rectangles are often used. Additionally, analysis methods for addressing pseudocapacitive behaviour, such as selectively analysing the linear section of the CV profile, can lead to an overestimation of the integral for the capacitive region. To eliminate those sources of variation, having an established protocol is crucial.

### 3.3. Long-term cycling analysis

The analysis of long-term GCD cycling data was optional. In this analysis, participating groups were asked to report the capacitance retention after 10,000 cycles (Fig. 7). Only 3 out of 14 groups could analyse all 10,000 charge-discharge cycles. All of these groups used a computational method to analyse the data. Several groups partially analysed the long-term cycling data, but did not report capacitance retention values. See the Supplementary Information for more details (SI Section 4.5).

Of the 3 groups who reported capacitance retention values, two chose to define this relative to the capacitance of the 1st cycle. In contrast, the other group defined this relative to the maximum capacitance obtained during the long-term cycling. In the future, we recommend that all groups report capacitance retention relative to the maximum capacitance to account for stabilisation of cycling. This is shown in Equation (8):



**Fig. 6.** Specific capacitance results ( $F g^{-1}$ ) collected from participating groups for (a) File 3 (ideal), where three distinctive groupings of reported values are seen, and (b) File 4 (non-ideal), where three groups of values are also present. The mean value for the upper group in File 3 is  $104.9 F g^{-1}$ . The mean value for the lower group in File 3 is  $26.0 F g^{-1}$ . The mean value for the upper group in File 4 is  $44.7 F g^{-1}$ . The adjusted mean value for the lower group in File 4 is  $10.8 F g^{-1}$ . The mean value for the middle group is not reported as these values have been calculated using incorrect equations.



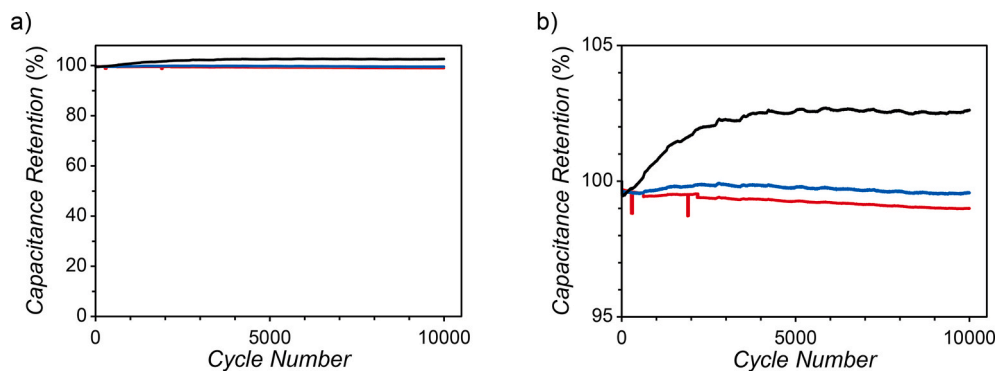


Fig. 7. (a) Capacitance retention data (%) from long-term GCD cycling data collected from participating groups. (b) A zoomed in view of the data.

$$\text{Capacitance Retention} = \frac{C_{nth \text{ cycle}}}{C_{max}} \times 100\% \quad (8)$$

where  $C_{nth \text{ cycle}}$  is the capacitance calculated for the  $n$ th cycle and  $C_{max}$  is the maximum capacitance achieved after stabilisation. This equation allows capacitance retention up to the  $n$ th cycle to be calculated. To allow more groups to obtain an in-depth observation of how performance changes over a long period, an accessible and standardised analysis program for long-term cycling data is required.

#### 4. Limitations

The scope of this study was limited to focus on the analysis of the most common techniques present in the wider literature and in industry. As a result, there are several limitations to this interlaboratory study. The most relevant ones are listed below:

1. Only two-electrode cell data were provided and analysed in this study, even though three-electrode cells are also widely used in research for supercapacitor devices to calculate the specific capacitance of electrode materials separately upon positive and negative charging [34].
2. For simplicity, Electrochemical impedance spectroscopy (EIS) data were not provided for determination of resistance.
3. The determination of internal resistance was not split into equivalent series resistance (ESR) and equivalent distribution resistance (EDR) [31].
4. As the participating groups were provided with datasets as measured in our laboratory, differences in electrode fabrication, cell assembly, and electrochemical measurements between laboratories were not assessed. Variations in the manufacturing process, including mass loading, electrode thickness, and pressurisation, can significantly affect device performance [46,47].

An extension of this study would include the analysis of three-electrode and EIS data. A follow-up study to assess how differences in cell assembly also impact reported performance between laboratories would provide further invaluable recommendations for reducing experimental variation between research groups.

#### 5. Recommendations for ideal and non-ideal supercapacitor datasets

Groups must employ correct formulae for electrochemical calculations and follow recommendations for the best practices for analysing and reporting data from the ideal supercapacitor energy storage devices. Here, we reiterate the standard formulae and the key recommendations as reflected by the current study (Table 1).

Additionally, it is important to reinforce the following:

Table 1

Recommended formulae for GCD and CV analysis for supercapacitor devices.

| Performance metric   | Galvanostatic charge-discharge (GCD)  | Cyclic voltammetry analysis (CV)  |
|----------------------|---|---|
| Total capacitance    | $C_T = \frac{I}{\left(\frac{\Delta V}{\Delta t}\right)}$  | $C_T = \frac{\int_{V_1}^{V_2} I dV}{(V_1 - V_2) \bullet v}$   |
| Capacity             | $\text{Capacity} = I \bullet \Delta t$  | $\text{Capacity} = \int_{V_1}^{V_2} I dt$   |
| Specific capacitance | Two-electrode cell:<br>$C_{g,1} = \frac{C_T}{M_{cell}}$<br>Pseudo single electrode:<br>$C_{g,2} = \frac{2C_T}{m_{ave}}$ | Two-electrode cell:<br>$C_{g,1} = \frac{C_T}{M_{cell}}$<br>Pseudo single electrode:<br>$C_{g,2} = \frac{2C_T}{m_{ave}}$ |
| Internal resistance  | $R = \frac{\Delta V}{2I}$   | N/A   |

1. When reporting specific capacitance, one should always make sure to clarify whether it is the specific capacitance of the electrode material in a two-electrode cell, or the specific capacitance of the electrode material independent of device architecture (i.e., a “pseudo” single electrode measurement). This recommendation was suggested by several participating groups in this study.
2. For devices displaying non-ideal behaviour, other performance metrics, such as capacity and discharge energy, need to be calculated and reported alongside any average capacitance values [42–44].
3. When using GCD datasets to calculate capacitance, the voltage range used to calculate the discharge slope should be reported, and the Ohmic voltage drop should be excluded from this calculation.
4. Where possible, GCD datasets should be used to calculate performance metrics instead of CV datasets.
5. Agreement and application of consistent criteria are necessary for accurate determination of the Ohmic voltage drop in GCD experiments.

#### 6. Conclusions

In this work, the first interlaboratory study on the analysis of supercapacitor data was conducted. This study shows that, while most of the participants reported similar results for different performance metrics calculated from GCD and CV datasets, some groups reported incorrect values due to the use of incorrect formulae during analysis. As a result, we remind the community of the correct analysis formulae to ensure more reliable reporting of performance metrics going forwards. In addition, different valid interpretations of “specific capacitance” between laboratories resulted in a range of values being reported for this performance metric. To avoid confusion going forwards, researchers should clarify their interpretation of “specific capacitance” when reporting values. This study also found that the impact of different practices in data analysis becomes more significant for electrochemical profiles showing less ideal capacitive behaviour. We support previous

recommendations that non-ideal datasets should not be analysed using formulae for ideal supercapacitors, in which charge is solely stored via non-Faradaic adsorption of ions in the electric double-layer, to avoid inaccurate reporting of performances, and capacity should be reported for such devices. In the future, establishing an accessible and standardised open-access analysis protocol for calculating performance metrics of fast-charging energy devices is required to improve the consistency of analysis and reporting. An agreed computational analysis program could benefit the community by further eliminating variations caused by subjectivity in manual analysis. Further efforts are recommended to consider the key findings of this study when developing, for example, an optimized machine-learning algorithm that automatically derives the relevant key data from various data files under different testing conditions. Such an “approved” tool, especially when being part of open science, would enormously reduce the variation seen from today’s use of individual approaches toward supercapacitor data analysis.

### CRedit authorship contribution statement

**Jamie W. Gittins:** Conceptualization, Methodology, Investigation, Visualization, Project administration, Writing – original draft, Writing – review & editing. **Yuan Chen:** Conceptualization, Methodology, Formal analysis, Data curation, Writing – original draft, Writing – review & editing. **Stefanie Arnold:** Formal analysis, Writing – review & editing. **Veronica Augustyn:** Writing – review & editing. **Andrea Balducci:** Writing – review & editing. **Thierry Brousse:** Formal analysis, Writing – review & editing. **Elzbieta Frackowiak:** Writing – review & editing. **Pedro Gómez-Romero:** Writing – review & editing. **Archana Kanwade:** Formal analysis, Writing – review & editing. **Lukas Köps:** Formal analysis, Writing – review & editing. **Plawan Kumar Jha:** Formal analysis, Writing – review & editing. **Dongxun Lyu:** Validation, Writing – review & editing. **Michele Meo:** Writing – review & editing. **Deepak Pandey:** Formal analysis, Writing – review & editing. **Le Pang:** Formal analysis, Writing – review & editing. **Volker Presser:** Writing – review & editing. **Mario Rapisarda:** Formal analysis, Writing – review & editing. **Daniel Rueda-García:** Formal analysis, Writing – review & editing. **Saeed Saeed:** Formal analysis, Writing – review & editing. **Parasharam M. Shirage:** Writing – review & editing. **Adam Ślesinski:** Formal analysis, Writing – review & editing. **Francesca Soavi:** Formal analysis, Funding acquisition, Writing – review & editing. **Jayan Thomas:** Writing – review & editing. **Maria-Magdalena Titirici:** Writing – review & editing. **Hongxia Wang:** Writing – review & editing. **Zhen Xu:** Formal analysis, Writing – review & editing. **Aiping Yu:** Writing – review & editing. **Maiwen Zhang:** Formal analysis, Writing – review & editing. **Alexander C. Forse:** Conceptualization, Methodology, Funding acquisition, Supervision, Writing – review & editing.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships with other people or organisations that could have inappropriately influenced the work reported in this paper.

### Data availability

The datasets that have been used in this study are freely available as Supplementary Data.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jpowsour.2023.233637>.

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