

Composition-Dependent Interfacial Resistance in Ex-Situ rGO/MnO₂ Nanocomposite Electrodes Prepared Using Tea-Stem Extract: An Impedance Spectroscopy Study

Cherin Virginia¹, Ngurah Ayu Ketut Umiati¹, Agus Subagio¹

¹Department of Physics,
Faculty of Science and Mathematics, Diponegoro University, Semarang, Indonesia,

Corresponding Author: Cherin Virginia

DOI: <https://doi.org/10.52403/ijrr.20261020>

ABSTRACT

Reduced graphene oxide (rGO) prepared using tea-stem extract as a green reducing agent was blended ex situ with manganese dioxide (MnO₂) at mass ratios of 1:3, 1:1, and 3:1. Impedance spectra collected over the frequency range of 100 kHz to 0.01 Hz were fitted using four equivalent circuits, which were evaluated based on residual error and the Bayesian information criterion (BIC). The classical Randles circuit incorporating a Warburg element was rejected because its residual error was 5.2–60 times greater than that of the modified Randles circuit, in which constant phase elements replaced the double-layer capacitor and the Warburg element. Moreover, the classical circuit yielded a charge-transfer resistance that collapsed to zero for the 1:1 composite. In the modified circuit, the series resistance increased from 39 to 302 Ω as the rGO fraction increased, whereas the charge-transfer resistance varied nonmonotonically, reaching 2.4, 14.8, and 1.8 k Ω for the 1:3, 1:1, and 3:1 composites, respectively. The 1:1 composite also exhibited a relaxation process 16–23 times slower than those of the other two composites. Across the three composites, voltammetric capacitance retention between scan rates of 10 and 100 mV s⁻¹ decreased

with increasing series resistance, whereas galvanostatic capacitance retention between current densities of 1 and 10 A g⁻¹ followed the trend in relaxation frequency. The low-frequency admittance of the diffusion-like element also followed the trend in specific capacitance. These findings distinguish ohmic, interfacial, and capacitive limitations and provide an impedance-based framework for designing green-synthesized composite electrodes.

Keywords: interfacial resistance; electrochemical impedance spectroscopy; reduced graphene oxide; manganese dioxide; tea-stem extract; supercapacitor

INTRODUCTION

Electrochemical capacitors bridge the gap between batteries and conventional capacitors by offering high power density and long cycle life. Their performance depends strongly on the electrode materials and their properties. [1,2] Carbon-based electrodes store charge primarily through electrical double-layer mechanisms, and graphene-derived carbons offer high electrical conductivity and accessible surface area for charge storage. [3] Transition-metal oxides contribute Faradaic pseudocapacitance. Among these materials,

manganese dioxide (MnO₂) is attractive because of its high theoretical capacitance, low cost, and natural abundance. However, its relatively poor electronic conductivity can limit its rate performance. [4] Combining MnO₂ with reduced graphene oxide (rGO) is therefore a widely investigated strategy for integrating a conductive carbon network with a pseudocapacitive phase. [5]

Graphene oxide (GO) is conventionally reduced using hydrazine and other chemical reducing agents, some of which pose environmental and safety concerns. These concerns have motivated the search for greener alternatives. [6] Aqueous plant extracts rich in polyphenols and other phytochemicals can facilitate GO reduction and help stabilize the resulting material. [7] Tea-stem (kukicha) extract is a promising, low-cost reducing agent because it is derived from tea processing. [8] Nevertheless, the effectiveness and reproducibility of plant-based reduction methods depend on the botanical source, extract composition, and synthesis conditions.

Previous studies of rGO/MnO₂ electrodes have generally evaluated the effects of composition in terms of specific capacitance and cycling stability. [9,10] Although these metrics are essential for assessing electrochemical performance, they do not independently identify the resistive processes that limit electrode response. Electrochemical impedance spectroscopy (EIS) can help distinguish ohmic and interfacial contributions and characterize frequency-dependent electrochemical behavior when the impedance spectra are analyzed using an appropriate equivalent circuit. [11] The classical Randles circuit represents the interfacial response using a charge-transfer resistance in series with a Warburg diffusion element, with this branch connected in parallel with the double-layer capacitance. [12] However, porous and heterogeneous composite electrodes rarely behave as ideal capacitive systems. Their non-ideal capacitive behavior is commonly represented using constant phase elements (CPEs), which account for the dispersion of

interfacial time constants. [13,14] Selecting an appropriate equivalent circuit is therefore essential because parameters obtained from an inadequate model may be poorly identifiable or physically ambiguous. Systematic comparisons of competing circuits, supported by quantitative model-selection criteria, can help establish whether the selected model adequately describes the measured impedance response. [15]

In this study, electrochemical impedance spectroscopy (EIS) was used to investigate the composition-dependent resistance of ex situ rGO/MnO₂ nanocomposite electrodes prepared using tea-stem extract as a green reducing agent. Three rGO₂ mass ratios were examined: 1:3, 1:1, and 3:1. Although the synthesis and capacitive performance of these materials were reported previously, [16] the present study focuses specifically on the analysis and interpretation of their electrochemical impedance data. The classical Randles circuit was quantitatively compared with alternative equivalent circuits incorporating constant phase elements to identify the model that best described the measured impedance spectra. The selected model was then used to examine how the composition affected the series resistance, charge-transfer resistance, and associated relaxation frequency. Finally, these impedance-derived parameters were compared with the scan-rate-dependent and current-density-dependent electrochemical responses of the same electrodes. To the best of our knowledge, a statistically guided comparison of equivalent-circuit models applied to tea-stem-extract-derived rGO/MnO₂ composites across different composition ratios has not previously been reported.

MATERIALS & METHODS

Materials

GO, rGO, MnO₂, and the composites were prepared as described previously. [16] GO was prepared from graphite by the Hummers method and reduced with an aqueous extract of tea-stems under alkaline conditions at 80 °C, followed by a hydrothermal step at 180

°C. MnO₂ was synthesized hydrothermally from KMnO₄ and HCl at 180 °C for 3 h. The composites were prepared ex situ by ultrasonic mixing of the two components in ethanol at rGO/MnO₂ mass ratios of 1:3, 1:1, and 3:1, followed by centrifugation, washing, and vacuum drying.

Electrode preparation and electrochemical measurements

A glassy carbon electrode (GCE, 3 mm diameter) was polished with alumina slurry, rinsed, and dried. Each composite was dispersed in a water–ethanol mixture by sonication, drop-cast on the GCE, and fixed with Nafion binder 5 µL. The active mass used was 0.1 mg.

Measurements were carried out with a PalmSens4 potentiostat in a three-electrode cell, with the modified GCE as working electrode, an Ag/AgCl reference electrode, and a platinum counter electrode in 1 M H₂SO₄. Cyclic voltammetry (CV) was recorded over a 1.0 V window (−0.2 to 0.8 V versus Ag/AgCl) at 10, 25, 50, 75, and 100 mV s^{−1}, and the specific capacitance was calculated from the integrated CV area. Galvanostatic charge–discharge (GCD) was performed in the same window at 10, 7.5, 5, 2.5, and 1 A g^{−1}, and the specific capacitance was $C_s = I\Delta t / (m\Delta V)$, where I is the discharge current (A), Δt the discharge time (s), m the active mass (g), and ΔV the potential window (V). EIS was measured at the open-circuit potential with a 10 mV sinusoidal signal from 100 kHz to 0.01 Hz (61 frequencies).

Equivalent-circuit analysis

Four equivalent circuits were compared (Figure 1 shows the modified circuit). Circuit A1 is the classical Randles circuit with an

ideal double-layer capacitor C and a semi-infinite Warburg element $Z_W = \sigma(1 - j)\omega^{-1/2}$ in series with R_{ct} (Eq. 1). Circuit A2 replaces C by a CPE. Circuit M, the modified Randles circuit, also replaces the Warburg element by a second CPE (Eq. 2). Circuit C contains two parallel resistor–CPE arcs in series (Eq. 3):

$$Z_{A1} = R_s + \frac{R_{ct} + Z_W}{1 + j\omega C (R_{ct} + Z_W)} \quad (1)$$

$$Z_M = R_s + \left[Q_1(j\omega)^{n1} + \frac{1}{R_{ct} + \frac{1}{Q_2(j\omega)^{n2}}} \right] \quad (2)$$

$$Z_C = R_s + \frac{R_{ct}}{1 + R_{ct} Q_1(j\omega)^{n1}} + \frac{R_d}{1 + R_d Q_2(j\omega)^{n2}} \quad (3)$$

Here R_s is the series resistance, R_{ct} the charge-transfer resistance, R_d a second interfacial resistance, ω the angular frequency, j the imaginary unit, and Q and n the coefficient and exponent of a CPE ($Z_{CPE} = 1/[Q(j\omega)^n]$). Spectra were fitted by complex nonlinear least squares (trust-region reflective algorithm, SciPy) minimizing the squared relative residuals of the real and imaginary parts, with 80 random starting points per circuit and bounded parameters. Parameter standard errors came from the Jacobian-based covariance matrix scaled by the reduced χ^2 . The fitting routine reproduced the parameters that the instrument software returned for circuit A1. Two quantities were derived from circuit M. The relaxation frequency of the interfacial arc, $f_c = 1/(2\pi\tau)$ with $\tau = (R_{ct} \cdot Q_1)^{1/n1}$, [16] and the low-frequency admittance of the diffusion-like element, $Y_2 = Q_2(2\pi \times 0.01)^{n2}$, evaluated at 0.01 Hz because the coefficients Q_2 of elements with different exponents are not directly comparable.

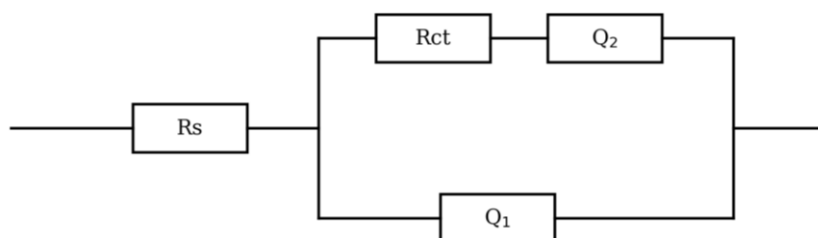


Figure 1. Modified Randles circuit (circuit M): series resistance R_s , followed by a constant phase element Q_1 in parallel with the series combination of the charge-transfer resistance R_{ct} and a second constant phase element Q_2 .

Statistical analysis

Model adequacy was judged by the reduced $\chi^2 = \frac{1}{2N-k} \sum_{i=1}^N \left[\left(\frac{\Delta Z'_i}{|Z_i|} \right)^2 + \left(\frac{\Delta Z''_i}{|Z_i|} \right)^2 \right]$ and by the Bayesian information criterion, $BIC = 2N \ln \left(\frac{RSS}{2N} \right) + k \ln(2N)$, [17] where $N = 61$ is the number of frequencies, k the number of parameters, and RSS the residual sum of squares. A BIC difference larger than 10 was taken as very strong evidence for the lower value. [18] CV retention was defined as the specific capacitance at 100 mV s⁻¹ divided by that at 10 mV s⁻¹, and GCD retention as the specific capacitance at 10 A g⁻¹ divided by that at 1 A g⁻¹. Because only three composites were compared, no inferential statistics were applied to the relationships between impedance descriptors and performance metrics; these were compared by rank order only.

RESULT

Experimental impedance response

The Nyquist plots Figure 2 and Bode plots Figure 3 showed that none of the three composites had the textbook Randles signature of a single semicircle followed by a 45° Warburg line and a near-vertical capacitive tail. The real-axis intercept at 100 kHz ranged from 40.9 Ω (1:3) to 304.9 Ω (3:1) in the same electrolyte and cell. The phase angle did not approach -90° in the measured range: at 0.01 Hz it was 62.4° (1:3), 49.6° (3:1), and 32.6° (1:1), and the impedance modulus at this frequency was 74.2, 48.7, and 16.0 kΩ for 1:3, 1:1, and 3:1. All composites showed two overlapping phase features, a maximum at intermediate frequency and a rise at low frequency Figure 3B. The 1:1 composite differed from the other two: its phase maximum (62.0°) occurred near 11 Hz and decayed at lower frequency, whereas the high-frequency feature of 1:3 lay more than one decade higher in frequency.

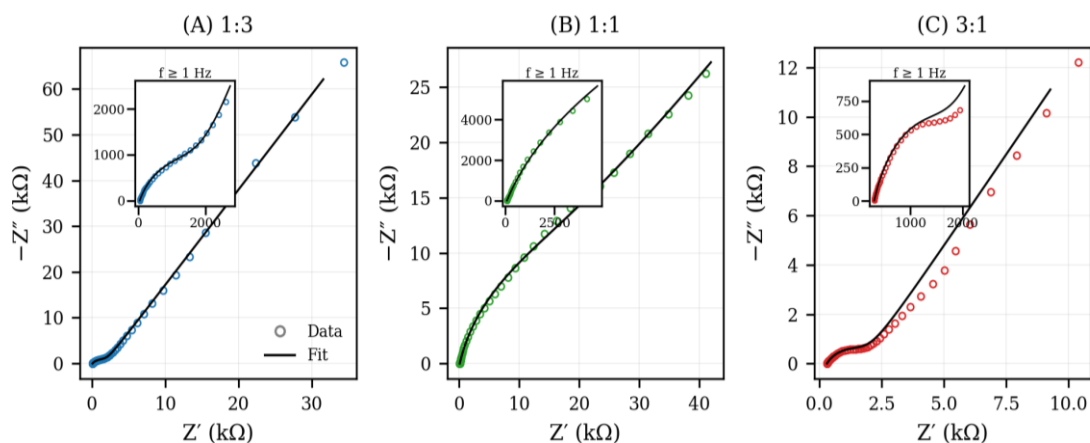


Figure 2. Nyquist plots of rGO/MnO₂ composites (A) 1:3, (B) 1:1, and (C) 3:1. Symbols are measured data and lines are fits of circuit M; insets show the region $f \geq 1$ Hz.

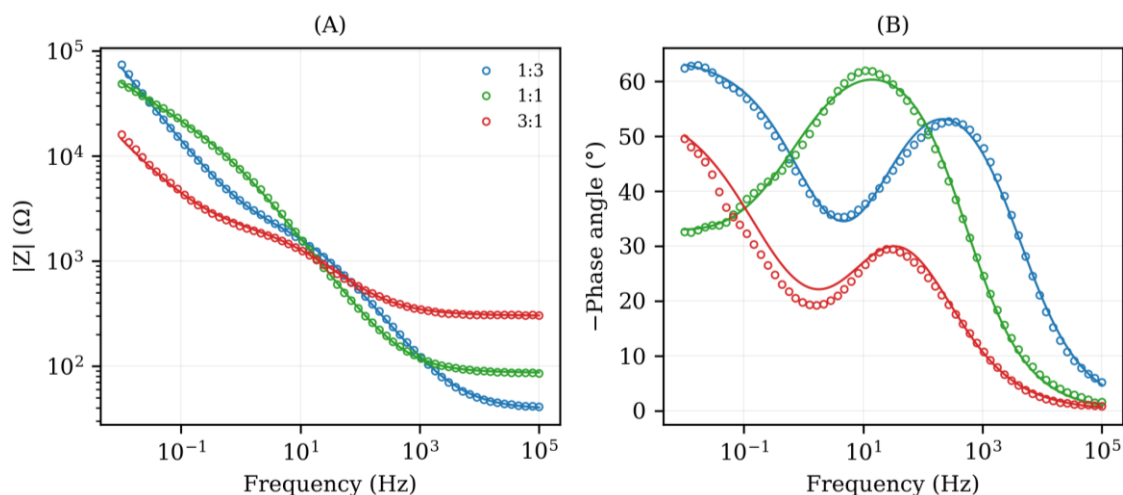


Figure 3. Bode plots of (A) impedance modulus and (B) phase angle of the three composites. Symbols are measured data and lines are fits of circuit M.

Classical Randles circuit

Fitting the classical Randles circuit (A1) with the instrument software gave the circuits and parameters in **Figure 4**. R_s from the fits agreed within 9% with the 100 kHz intercept, but the charge-transfer resistance of the 1:1

composite collapsed to a value far below 0.03 Ω , which is the lower limit of the fit and has no physical meaning. The fitting routine used here returned the same values as the software, and the relative standard error of R_{ct} of 1:1 was far above 100%.

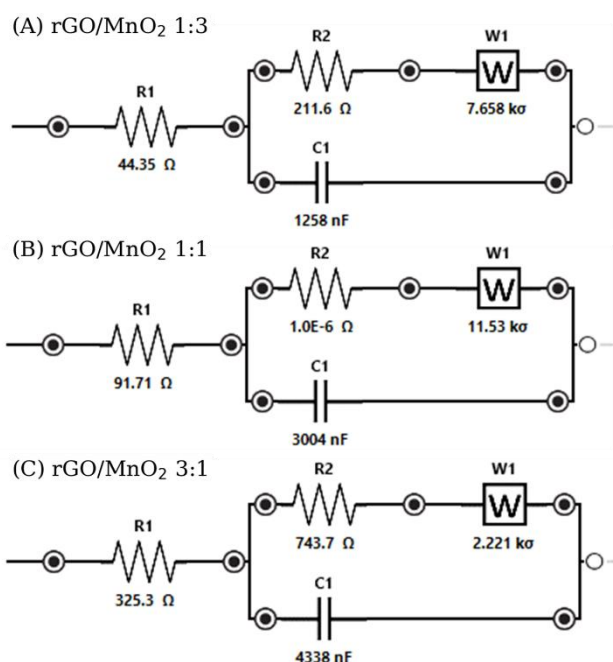


Figure 4. Classical Randles–Warburg circuits (circuit A1) fitted to the impedance spectra of the rGO/MnO₂ composites (A) 1:3, (B) 1:1, and (C) 3:1. R_1 is the series resistance, the resistor in the parallel branch the charge-transfer resistance, C_1 the double-layer capacitance, and W_1 the Warburg coefficient ($k\Omega s^{-1/2}$).

Discrimination between equivalent circuits

Circuit A1 gave the largest residual error for every composite **Table 1**. Its reduced χ^2 was 5.2 to 60 times larger than that of circuit M,

and its BIC was higher by 194 to 493 units, far above the threshold of 10. Replacing the capacitor by a CPE (A2) brought the fit close to circuit M only for 1:1 (χ^2 1.6 times larger) and not for 1:3 (reduced $\chi^2 = 1.4 \times 10^{-2}$, with

relative standard errors of about 30% for R_{ct} and Q) or 3:1. The two-arc circuit C lowered the BIC only for 3:1 and only marginally, and its parameters were poorly defined: the second resistance had a relative standard error of 90% for 1:3, and R_{ct} of 3:1 had an uncertainty of 29%. Circuit M was therefore

the minimal circuit that described all three composites with well-conditioned parameters (relative standard errors of 8% or less; **Table 2**). It reproduced the spectra of 1:3 and 1:1 closely, whereas 3:1 showed systematic deviations confined mainly to the lowest frequencies **Figures 2 and 3**.

Table 1. Fit quality of the equivalent circuits (reduced χ^2 and difference in BIC relative to circuit M; positive values favour circuit M).

Sample	χ^2 (A1)	χ^2 (A2)	χ^2 (M)	χ^2 (C)	Δ BIC (A1)	Δ BIC (A2)	Δ BIC (C)
1:3	1.72×10^{-2}	1.36×10^{-2}	2.84×10^{-4}	2.97×10^{-4}	493	468	9
1:1	1.21×10^{-2}	4.27×10^{-4}	2.62×10^{-4}	3.93×10^{-4}	460	56	53
3:1	5.55×10^{-3}	2.68×10^{-3}	1.06×10^{-3}	9.60×10^{-4}	194	109	-9

Circuit C has a lower BIC than circuit M only for 3:1 (negative Δ BIC), where R_{ct} was uncertain, and its second resistance was unidentifiable for 1:3.

Parameters of the modified Randles circuit

Table 2 lists the parameters of circuit M. R_s rose monotonically along the ratio series, by a factor of 7.8 from 1:3 to 3:1. R_{ct} was non-monotonic and 6.1 and 8.0 times larger for

1:1 than for 1:3 and 3:1, and the relaxation frequency of 1:1 was 16 to 23 times lower than that of the other two composites. The exponents were $n_1 = 0.67$ – 0.75 and $n_2 = 0.39$ – 0.71 , and Y_2 increased monotonically from 1:3 to 3:1.

Table 2. Parameters of the modified Randles circuit (circuit M), with relative standard errors (%) in parentheses, and derived quantities.

Sample	R_s (Ω)	R_{ct} ($k\Omega$)	Q_1	n_1	Q_2	n_2	f_c (Hz)	Y_2
1:3	38.7 (1)	2.44 (2)	1.70 (2)	0.725 (<1)	8.8 (1)	0.713 (<1)	12.8	1.22
1:1	86.3 (<1)	14.83 (7)	2.64 (2)	0.750 (<1)	6.7 (5)	0.395 (3)	0.55	2.23
3:1	301.7 (1)	1.85 (4)	3.77 (8)	0.666 (2)	38.5 (2)	0.621 (2)	8.7	6.91

Electrochemical performance metrics

Table 3 lists the performance metrics of the same electrodes. At 1 A g^{-1} , C_s increased along the ratio series by a factor of 9.5 (1:3

to 3:1). GCD retention was similar for 1:3 and 3:1 and much lower for 1:1, whereas CV retention decreased from 1:3 to 3:1.

Table 3. Performance metrics of the composites.

Sample	C_s (GCD, 1 A g^{-1})	C_s (GCD, 10 A g^{-1})	GCD retention (%)	C_s (CV, 10 mV s^{-1})	C_s (CV, 100 mV s^{-1})	CV retention (%)
1:3	66.5	31.3	47.0	41.30	11.90	28.8
1:1	189.9	15.4	8.1	47.98	7.05	14.7
3:1	629.0	292.0	46.4	278.32	33.95	12.2

Relation between impedance descriptors and performance

Across the three composites, the descriptors and the metrics changed in the same order **Figure 5**. CV retention decreased monotonically as R_s increased (**Figure 5A**). GCD retention followed the order of f_c ($1:3 >$

$3:1 > 1:1$; **Figure 5B**), and C_s at 1 A g^{-1} followed the order of Y_2 ($1:3 < 1:1 < 3:1$; **Figure 5C**). With three composites, a rank correlation cannot be significant (the smallest attainable exact two-sided p is 0.33), so these observations are descriptive.

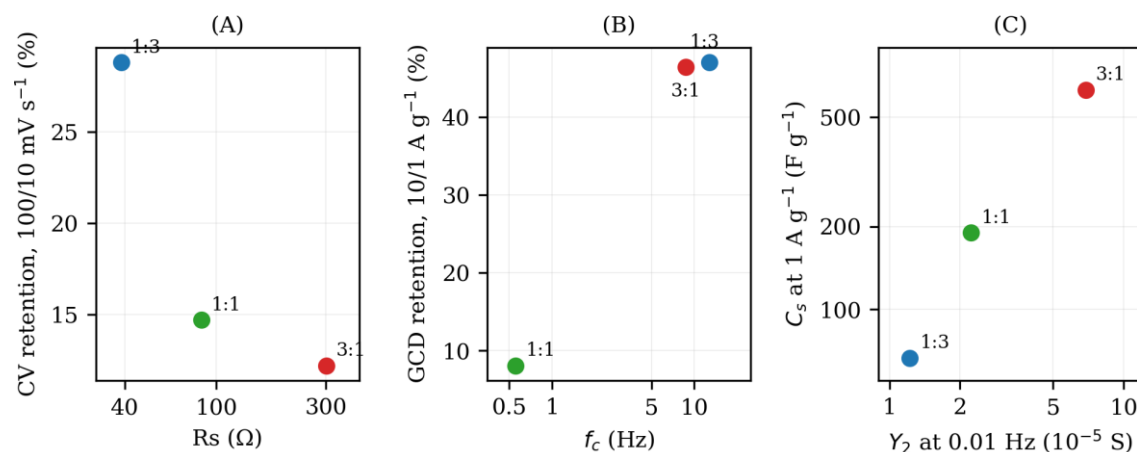


Figure 5. Relation between impedance descriptors and performance of the three composites: (A) CV retention versus R_s , (B) GCD retention versus f_c , and (C) specific capacitance at 1 A g⁻¹ versus Y_2 .

DISCUSSION

The semi-infinite Warburg element presupposes a planar interface and one unrestricted diffusion process, which is not the situation in a porous, drop-cast composite film. The exponents of the interfacial arc ($n_1 = 0.67$ – 0.75) and of the diffusion-like element ($n_2 = 0.39$ – 0.71) lay far below the ideal capacitive value of 1, and exponents of this kind are commonly attributed to a distribution of interfacial time constants and to distributed ion penetration in porous films. [19,20] Retaining the Randles topology but using CPEs (circuit M) gave identifiable parameters for all composites, whereas the classical circuit returned a charge-transfer resistance of zero for 1:1. The practical lesson is that R_{ct} and Warburg coefficients from a Randles fit should be reported only after the circuit has been tested against alternatives. [21]

The electrolyte and cell were identical for all measurements, so the 7.8-fold increase of R_s from 1:3 to 3:1 must come from the electrode film and its contact with the glassy carbon substrate. A larger fraction of conductive carbon would be expected to lower R_s , so the intrinsic conductivity of the carbon cannot be the controlling factor. [22] Film uniformity, thickness, and contact quality in drop-cast ex-situ films are the more likely controls, but they were not measured separately. [14] A series resistance of this size shifts the effective potential by the product of current

and R_s and compresses the potentiodynamic response at high scan rate, which is consistent with the decrease of CV retention as R_s increased (Figure 5A).

Both neighbouring compositions relaxed with f_c of 8.7–12.8 Hz, whereas 1:1 relaxed at 0.55 Hz, had the largest R_{ct} , and retained only 8% of its capacitance between 1 and 10 A g⁻¹. Its n_2 of 0.39 and the fall of its phase angle to 32.6° at 0.01 Hz show that its low-frequency response also departs from both capacitive and diffusive ideals. [23] A plausible explanation is that, at this intermediate composition, [24] the carbon sheets and the oxide are poorly interconnected and part of the active oxide is isolated from the conductive network. [25] This is a working hypothesis that requires direct evidence, for example conductivity measurements, surface-area measurements, and cross-sectional microscopy of the same electrodes, which were not part of this study. The 1:3 and 3:1 composites had similar f_c and nearly identical GCD retention (47% and 46%), yet their C_s at 1 A g⁻¹ differed by a factor of 9.5. The composite with the lowest nominal MnO₂ fraction (3:1, 25% by mass) therefore stored the most charge, [26] whereas the MnO₂-rich 1:3 composite (75%) had the lowest C_s and the lowest Y_2 , a pattern consistent with a low utilization of MnO₂ at 1:3. Y_2 and C_s followed the same order across the three composites (Figure 5C), this agreement supports Y_2 as a compact

impedance indicator of capacity, [27] although its physical meaning needs confirmation with more compositions. [28] The 3:1 composite kept 46% of its capacitance in GCD (1 to 10 A g⁻¹) but only 12% in CV (10 to 100 mV s⁻¹). CV retention followed the series resistance, whereas f_c paralleled the GCD behavior. [29,30] Impedance descriptors should therefore be matched to the measurement protocol of interest and not reduced to a single resistance. [31]

The statistically screened circuit and the triple of descriptors (R_s , f_c , Y_2) formed a compact fingerprint that separated the three compositions: 1:3 combined low R_s and fast relaxation with low admittance, 1:1 was interfacially limited, and 3:1 combined the highest admittance and fast relaxation with the highest R_s . [32,33] Reducing the series resistance of the 3:1 electrode, for example by film thickness, loading, or contact optimization, is the most direct route to improve its high-rate response, and the 1:1 ratio is best avoided. [34,35] To the best of our knowledge, such a model-discriminated, composition-resolved impedance analysis has not been reported for tea-stem-reduced rGO/MnO₂, and the protocol can be transferred to other green-reduced carbon-oxide systems. [36]

Only three compositions were compared and each was represented by a single electrode, so electrode-to-electrode variability was not quantified and the observed orderings carry no statistical weight. [37] The active mass was about 0.1 mg, so the absolute capacitances carry a large uncertainty and the conclusions rely on relative trends. [38,39] The spectra were not tested for Kramers–Kronig consistency. [33,40] R_{ct} of 1:1 came from a partial arc, and the fit of 3:1 deviated systematically at low frequency, so these values are less certain than their standard errors suggest. [41] The explanations offered for the origin of the resistances are hypotheses that require microstructural characterization. [42]

CONCLUSION

The modified Randles circuit, in which constant phase elements replace the capacitor and the Warburg element, described the three tea-stem-reduced rGO/MnO₂ composites with identifiable parameters, whereas the classical Randles circuit did not (residual error 5.2 to 60 times larger, charge-transfer resistance of zero for 1:1). Along the ratio series (1:3, 1:1, 3:1), the series resistance increased 7.8-fold, while the charge-transfer resistance and relaxation frequency were non-monotonic, with the 1:1 composite as an interfacial bottleneck ($R_{ct} = 14.8$ k Ω ; $f_c = 0.55$ Hz). Retention of the CV response decreased with the series resistance, and the low-frequency admittance followed the capacitance. Capacity and kinetics were thus governed by different circuit elements, and the 3:1 composite would benefit most from a lower series resistance. These observations need confirmation with replicate electrodes, more compositions, and direct microstructural evidence.

Declaration by Authors

Acknowledgement: None

Source of Funding: None

Conflict of Interest: No conflicts of interest declared.

Creative Commons Attribution License 4.0

This is an open-access article published under the terms of the Creative Commons Attribution 4.0 International License (CC BY 4.0).

<https://creativecommons.org/licenses/by/4.0>

REFERENCES

1. Li S, Li Z. Flexible asymmetric supercapacitors constructed by reduced graphene oxide/MoO₃ and MnO₂ electrochemically deposited on carbon cloth. *Molecules*. 2024;29(13):3116. <https://doi.org/10.3390/molecules29133116>
2. Li X, Xu X, Xia F, et al. Electrochemically active MnO₂/RGO nanocomposites using Mn powder as the reducing agent of GO and the MnO₂ precursor. *Electrochimica Acta*. 2014; 130:305-313. <https://doi.org/10.1016/j.electacta.2014.03.040>

3. Chen X, Paul R, Dai L. Carbon-based supercapacitors for efficient energy storage. *National Science Review*. 2017;4(3):453-489. <https://doi.org/10.1093/nsr/nwx009>
4. Iqbal MZ, Aziz U, Siddique S, et al. Effect of distinct organic ligands on hierarchical porous manganese-based MOFs for battery-supercapacitor hybrid. *Materials Science in Semiconductor Processing*. 2023; 162:107511. <https://doi.org/10.1016/j.mssp.2023.107511>
5. Aleena A, Asadullah A, Khan A, et al. MnO₂-decorated rGO: a functional material for Congo Red dye removal. *Green Chemistry Letters and Reviews*. 2025;18(1):2542391. <https://doi.org/10.1080/17518253.2025.2542391>
6. Reddy BJ, Vickraman P, Justin AS. Facile green route synthesis of reduced graphene oxide through green reducing agents for supercapacitors. *AIP Conference Proceedings*. 2019;2115(1):030534. <https://doi.org/10.1063/1.5113373>
7. Saputra AMA, Marpongahtun, Andriyani, et al. Facile synthesis of reduced graphene oxide using natural plant extracts as green reducing agents. *Journal of King Saud University - Engineering Sciences*. 2025; 37:5. <https://doi.org/10.1007/s44444-025-00007-9>
8. Zhang W, Guo W, He C, et al. Exploring the quality and application potential of the remaining tea stems after the postharvest tea leaves: the example of Lu'an Guapian tea (*Camellia sinensis* L.). *Foods*. 2022;11(15):2357. <https://doi.org/10.3390/foods11152357>
9. Usharani B, Manivannan V. Hydrothermal synthesis of rGO-MnO₂ nanocomposite: characterization and in vitro biological evaluation. *Materials Letters: X*. 2022; 15:100162. <https://doi.org/10.1016/j.mlblux.2022.100162>
10. Salamon J, Simi A, Joy Prabu H, et al. Synthesis and characterization of rGO-anchored MnO₂ nanorods and their application in supercapacitors as electrode material. *Journal of Electronic Materials*. 2025;54(1):510-522. <https://doi.org/10.1007/s11664-024-11562-3>
11. Nitesh P, Sengottaiyan C, Ambikeswari N, et al. Insights into the regulation of interfacial charge distribution in ZnS@CoNi₂S₄ heterojunctions for high energy density supercapattery and efficient electrocatalytic water splitting applications. *Journal of Power Sources*. 2025; 642:236978. <https://doi.org/10.1016/j.jpowsour.2025.236978>
12. Hardianto YP, Shah SS, Shuaibu AD, et al. Modeling supercapacitors with the simplified Randles circuit: analyzing electrochemical behavior through cyclic voltammetry and galvanostatic charge-discharge. *Electrochimica Acta*. 2025; 513:145552. <https://doi.org/10.1016/j.electacta.2024.145552>
13. Zhao J, Gorbатовski G, Oll O, et al. Analysis of impedance: the distribution of capacitance in halide ion treated supercapacitors. *Journal of Electroanalytical Chemistry*. 2022; 922:116754. <https://doi.org/10.1016/j.jelechem.2022.116754>
14. Kim SH, Choi W. A method for performance evaluation and optimal sizing of the supercapacitor module by electrochemical impedance spectroscopy. In: INTELEC, International Telecommunications Energy Conference (Proceedings); 2009. <https://doi.org/10.1109/INTLEC.2009.5351800>
15. Navalpotro P, Anderson M, Marcilla R, Palma J. Insights into the energy storage mechanism of hybrid supercapacitors with redox electrolytes by electrochemical impedance spectroscopy. *Electrochimica Acta*. 2018; 263:110-117. <https://doi.org/10.1016/j.electacta.2017.12.167>
16. Qudsiyah RA, Taufiq HR, Priyono P, et al. Green hydrothermal synthesis of rGO/MnO₂ nanocomposites from *Musa paradisiaca* Linn. peel extract for high-performance supercapacitor electrodes. *Trends in Sciences*. 2026;23(7):12607. <https://doi.org/10.48048/tis.2026.12607>
17. Lobato-Peralta DR, Okoye PU, Alegre C. A review on carbon materials for electrochemical energy storage applications: state of the art, implementation, and synergy with metallic compounds for supercapacitor and battery electrodes. *Journal of Power Sources*. 2024; 617:235140. <https://doi.org/10.1016/j.jpowsour.2024.235140>

18. Lin ZH, Chen PJ. Evaluation and trend of smart clothing research: visualization analysis based on bibliometric analysis and quantitative statistics. *Fibers and Polymers*. 2024;25(4):1479-1511. <https://doi.org/10.1007/s12221-024-00521-8>
19. Rahmanabadi F, Sangpour P, Sabouri-Dodaran AA. Electrochemical deposition of MnO₂/RGO nanocomposite thin film: enhanced supercapacitor behavior. *Journal of Electronic Materials*. 2019;48(9):5813-5820. <https://doi.org/10.1007/s11664-019-07361-w>
20. Bekhit SM, Metwally W, Mohamed SG, et al. Electrodeposition of nickel selenides thin films for high-performance hybrid supercapacitor. *Journal of Energy Storage*. 2024; 83:110744. <https://doi.org/10.1016/j.est.2024.110744>
21. Ahmed M, Ahmed N, Ahmad H, et al. A comparative study on exploring sputtered titanium nitride thin films for high-performance supercapacitors. *Journal of Energy Storage*. 2025; 105:114712. <https://doi.org/10.1016/j.est.2024.114712>
22. Fernández-Sánchez C, McNeil CJ, Rawson K. Electrochemical impedance spectroscopy studies of polymer degradation: application to biosensor development. *TrAC Trends in Analytical Chemistry*. 2005;24(1):37-48. <https://doi.org/10.1016/j.trac.2004.08.010>
23. Sharma S, Chand P. Supercapacitor and electrochemical techniques: a brief review. *Results in Chemistry*. 2023; 5:100885. <https://doi.org/10.1016/j.rechem.2023.100885>
24. Patrick JSJ, Sankar M, Ruban MJR, et al. Interlacing rod and sphere morphology of MnO₂ in RGO/NiO/MnO₂ ternary nanocomposites for supercapacitive applications. *Journal of The Electrochemical Society*. 2022;169(12):123505. <https://doi.org/10.1149/1945-7111/aca8d0>
25. Conway BE. *Electrochemical supercapacitors*. New York: Springer US; 1999. <https://doi.org/10.1007/978-1-4757-3058-6>
26. Saravanan A, Arunachalam P, Reddy GR, Vijayan V. Development of MnO₂/rGO composite electrodes for enhanced electrochemical supercapacitor performance. *Journal of New Materials for Electrochemical Systems*. 2024;27(3):208-214. <https://doi.org/10.14447/jnmes.v27i3.a06>
27. Ingole SM, Navale ST, Navale YH, et al. Galvanostatically electroplated MnO₂ nanoplate-type electrode for potential electrochemical pseudocapacitor application. *Journal of Solid State Electrochemistry*. 2017;21(6):1817-1826. <https://doi.org/10.1007/s10008-017-3557-8>
28. Ke Q, Zhang Y, Fu Y, et al. Study on electrochemical performance of MnO@rGO/carbon fabric-based wearable supercapacitors. *Materials*. 2023;16(13):4687. <https://doi.org/10.3390/ma16134687>
29. Chebrolu VT, Jang D, Rani GM, et al. Overview of emerging catalytic materials for electrochemical green ammonia synthesis and process. *Carbon Energy*. 2023;5:e361. <https://doi.org/10.1002/cey2.361>
30. Le TH, Ngo VH, Nguyen MT, et al. Enhanced electrochemical performance of porous carbon derived from cornstalks for supercapacitor applications. *Journal of Electronic Materials*. 2021;50(12):6854-6861. <https://doi.org/10.1007/s11664-021-09249-0>
31. Ali M, Afzal AM, Iqbal MW, et al. Synthesis and analysis of the impact of rGO on the structural and electrochemical performance of CoMnS for high-performance energy storage device. *FlatChem*. 2023; 40:100518. <https://doi.org/10.1016/j.flatc.2023.100518>
32. Soren S, Chakroborty S, Pal K. Enhanced in tuning of photochemical and electrochemical responses of inorganic metal oxide nanoparticles via rGO frameworks (MO/rGO): a comprehensive review. *Materials Science and Engineering: B*. 2022; 278:115632. <https://doi.org/10.1016/j.mseb.2022.115632>
33. Ates M, Kuzgun O, Yildirim M, et al. rGO/MnO₂/polyterthiophene ternary composite: pore size control, electrochemical supercapacitor behavior and equivalent circuit model analysis. *Journal of Polymer Research*. 2020;27(8):202. <https://doi.org/10.1007/s10965-020-02183-5>
34. Godlaveeti SK, Maseed H, Reddy SA, et al. Electrochemical performance of ternary RGO/β-Ni (OH)₂/CeO₂ composite in addition with different metal oxides for supercapacitor application. *Advances in Natural Sciences: Nanoscience and Nanotechnology*. 2020;11(2):025021. <https://doi.org/10.1088/2043-6254/ab8bde>

35. Pimklang T, Watthanaphanit A, Hemnon W, et al. Selective phase control and enhanced electrochemical performance of rGO-MnO₂ nanocomposites for supercapacitor electrodes via solution plasma process: a greener alternative to hydrothermal process. *Materials Chemistry and Physics*. 2025; 341:130948. <https://doi.org/10.1016/j.matchemphys.2025.130948>
36. Imran M, Yasmeen A, Aslam M, et al. Advanced rGO@CNTs@MnSrS nanocomposite for supercapattery and electrochemical sensor. *Diamond and Related Materials*. 2024; 147:111372. <https://doi.org/10.1016/j.diamond.2024.111372>
37. Rondiya SR, Karbhal I, Jadhav CD, et al. Uncovering the origin of enhanced field emission properties of rGO-MnO₂ heterostructures: a synergistic experimental and computational investigation. *RSC Advances*. 2020; 10:25988-25998. <https://doi.org/10.1039/d0ra03360j>
38. Tarek YA, Shakil R, Reaz AH, et al. Wrinkled flower-like rGO intercalated with Ni(OH)₂ and MnO₂ as high-performing supercapacitor electrode. *ACS Omega*. 2022;7(23):20145-20154. <https://doi.org/10.1021/acsomega.2c01986>
39. Arunpandian M, Selvakumar K, Nagarajan ER, et al. Evaluation of rGO-decorated MnO₂/NiO nanocomposite for high-performance photocatalytic and supercapacitor applications. *Diamond and Related Materials*. 2023; 139:110383. <https://doi.org/10.1016/j.diamond.2023.110383>
40. Tarek YA, Shakil R, Roy CK, et al. Redox-mediated neutral electrolyte solution for high-performing Ni(OH)₂-MnO₂-rGO supercapacitor electrode. *ECS Transactions*. 2022;107(1):13429-13438. <https://doi.org/10.1149/10701.13429ecst>
41. Shan X, Wang L, Li L, et al. Hydrothermal regulation of MnO₂ on a wood-based RGO composite for achieving wide voltage windows and high energy density supercapacitors. *iScience*. 2024;27(3):109228. <https://doi.org/10.1016/j.isci.2024.109228>
42. Sen P, Rana S, De A. Hierarchical design of rGO-PEDOT-δ-MnO₂ nanocomposite for supercapacitors. *Journal of Electronic Materials*. 2020;49(1):763-772. <https://doi.org/10.1007/s11664-019-07794-3>

How to cite this article: Cherin Virginia, Ngurah Ayu Ketut Umiati, Agus Subagio. Composition-dependent interfacial resistance in ex-situ rGO/MnO₂ nanocomposite electrodes prepared using tea-stem extract: an impedance spectroscopy study. *International Journal of Research and Review*. 2026; 13(10): 222-232. DOI: <https://doi.org/10.52403/ijrr.20261020>
