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Automated Response Surface Methodology: Computational Replication and Validation Framework for Optimizing Supercapattery Materials †

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Abstract

Combining Response Surface Methodology (RSM) with Central Composite Design (CCD) is a powerful statistical approach to optimizing materials in energy storage systems. This study presents an open-source Python (v3.8+) framework that replicates and validates the RSM-based optimization of $NiCo_2S_4$–graphene supercapattery materials. We validated the framework by replicating a 20-experiment CCD analyzing graphene/NCS ratios, hydrothermal time, and S/Ni molar ratios. Advanced optimization using the Differential Evolution algorithm was integrated to efficiently solve the high-dimensional response surface space. The model explained 97.16% of the variance, and comprehensive diagnostic tests confirmed the assumptions of normality and residual independence. This approach provides an open-source methodology that supports reproducible and scalable data-driven material design and facilitates transparent computational materials science studies.

Keywords: synthesis parameters; process sensitivity; predictive capability; convergence behavior; hybrid capacitors; high-throughput screening; digital twin; intelligent experimentation; electrode architectures

1. Introduction

This article is a revised and expanded version of a paper entitled Python-Based Automated Response Surface Methodology: Computational Replication and Validation Framework for Supercapattery Materials Optimization, which was presented at The 1st International Online Conference on Designs.

Combining Response Surface Methodology (RSM) with Central Composite Design (CCD) is a powerful statistical approach to material optimization in energy storage systems [1,2]. RSM has been extensively applied in materials science to efficiently explore design spaces and identify optimal synthesis conditions, reducing experimental burden while maintaining rigor [2]. Recent computational advances have enabled significant progress in battery and supercapacitor research, including predictive modeling of graphite anode capacity fading [3] and automated design for efficient lithium-ion battery material separation and recycling [4].

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This study presents an open-source, Python-based computational framework for the automated analysis of RSM experiments, designed to scale to high-dimensional problems. We validate this framework by replicating the optimization of $NiCo_2S_4$–graphene hybrids originally reported by Hong et al. [1]. By reconstructing the statistical models and ANOVA tables, performing temporal residual diagnostics, and executing response surface optimization using transparent code, we aim to demonstrate the reliability of automated computational replication and provide a tool for future data-driven material design. The conceptual framework of this research, bridging experimental data with computational tools, is illustrated in Figure 1.

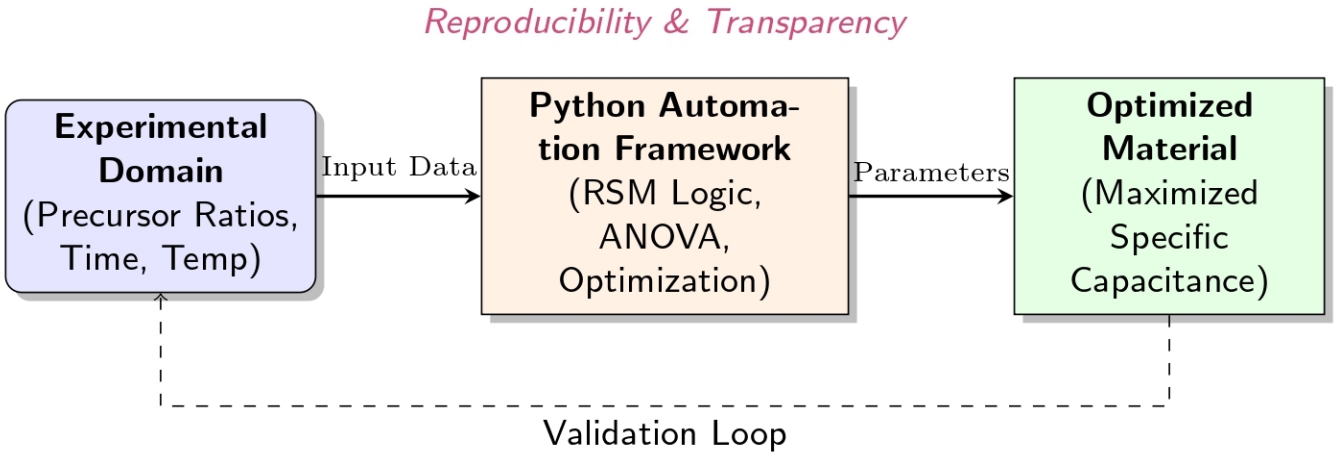


Figure 1. Conceptual framework of this study, integrating experimental design with Python-based automated statistical analysis to support material optimization and improve reproducibility.

The preliminary concepts of this computational framework were initially introduced in our previous conference abstract [5] and are herein fully expanded with detailed statistical validation, the integration of global optimization routines (Differential Evolution), and the complete Python source code.

2. Materials and Methods

2.1. Experimental Design and Data Acquisition

The dataset utilized in this computational replication was derived from the study by Hong et al. [1], which focused on optimizing the hydrothermal synthesis of $NiCo_2S_4$–graphene hybrids. A Central Composite Design (CCD) with five levels was employed. The design matrix consisted of 20 experimental runs, including 8 factorial points, 6 axial points (with $\alpha = 1.682$), and 6 center points to estimate pure error.

The independent variables (factors) investigated were as follows:

- X_1—Graphene/NCS mass ratio (%), ranging from 0.6% to 7.4%;
- X_2—Hydrothermal reaction time (h), ranging from 4.6 h to 11.4 h;
- X_3—Sulfur/Nickel (S/Ni) molar ratio, ranging from 3.3 to 6.7.

The response variable (Y) was the specific capacitance (F/g) measured at a current density of 1 A/g.

2.2. Computational Framework and Statistical Modeling

The automated analysis was developed entirely in Python (v3.8+), utilizing the 'pandas' and 'numpy' libraries for data manipulation, 'scipy.stats' for probabilistic calculations, 'scipy.optimize' for high-dimensional optimization, and 'matplotlib' for visualization. The workflow implemented in the code is detailed in Figure 2.

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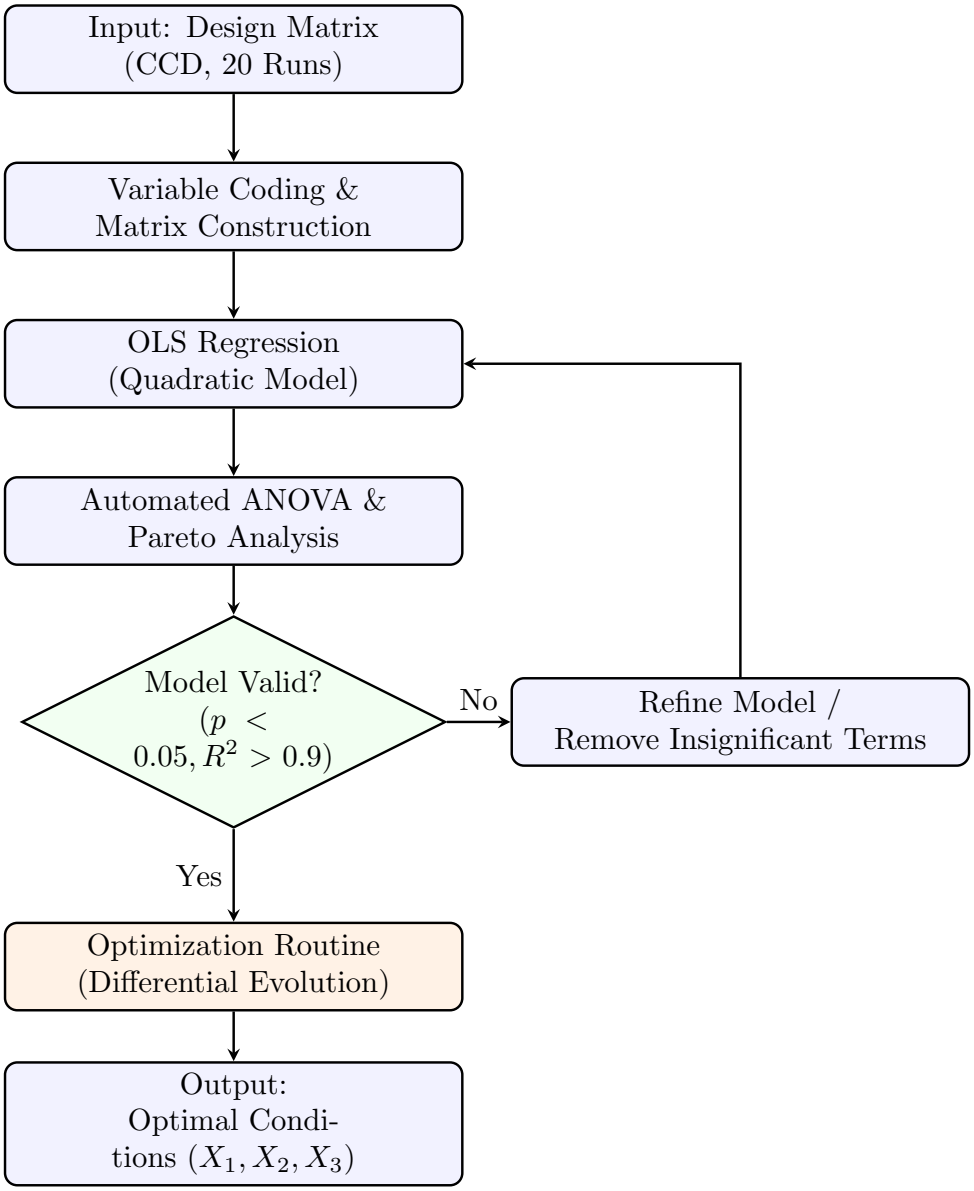


Figure 2. Flowchart of the Python-based automated methodology for RSM analysis incorporating advanced optimization.

A second-order polynomial equation (Equation (1)) was fitted to the experimental data using Multiple Linear Regression (MLR) via the Ordinary Least Squares (OLS) method:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} \beta_{ij} X_i X_j + \varepsilon \quad (1)$$

where Y is the predicted response; X_i denotes the coded independent variables; β_0 is the intercept; β_i, β_{ii}, and β_{ij} are the linear, quadratic, and interaction coefficients, respectively; and ε is the error.

The coefficients in Equation (1) have fundamental physicochemical interpretations. Linear coefficients (β_i) represent the primary effects of individual factors on the response. Interaction coefficients (β_{ij}) indicate synergistic or antagonistic effects between two parameters—for example, how sulfur concentration influences the incorporation of graphene in the $NiCo_2S_4$ matrix. Quadratic coefficients (β_{ii}) describe the curvature of the response space,

often reflecting threshold limits or material saturation effects where excessive increases in a variable begin to reduce capacitance.

Model adequacy was assessed through analysis of variance (ANOVA). Significance of regression terms was determined by the *F*-test and *p*-values ($\alpha = 0.05$). Using this framework, we conducted a lack-of-fit test and determined the Durbin–Watson statistic for run-order residual independence. For optimization, the classic grid-search algorithm was combined with the Differential Evolution (DE) algorithm—a metaheuristic for global optimization in continuous spaces—to support scalability for high-dimensional scenarios.

3. Results

3.1. Model Fitting and Statistical Analysis

The experimental results and the complete design matrix are presented in Table 1. The computational framework successfully fitted the quadratic model to the specific capacitance data. The regression yielded a high coefficient of determination ($R^2 = 0.9716$) and an adjusted R^2 of 0.9460, indicating that the model explains over 97% of the variability in the synthesis process.

Table 1. Complete experimental design matrix (CCD) and response (specific capacitance).

Trial	X_1 (Coded)	X_2 (Coded)	X_3 (Coded)	G/NCS (%)	Time (h)	S/Ni	Cap. (F/g)
1	−1	−1	−1	2.0	6.0	4.0	1040
2	−1	−1	1	2.0	6.0	6.0	840
3	−1	1	−1	2.0	10.0	4.0	801
4	−1	1	1	2.0	10.0	6.0	1033
5	1	−1	−1	6.0	6.0	4.0	1704
6	1	−1	1	6.0	6.0	6.0	1920
7	1	1	−1	6.0	10.0	4.0	1500
8	1	1	1	6.0	10.0	6.0	2380
9	−1.682	0	0	0.6	8.0	5.0	450
10	1.682	0	0	7.4	8.0	5.0	1660
11	0	−1.682	0	4.0	4.6	5.0	1570
12	0	1.682	0	4.0	11.4	5.0	1460
13	0	0	−1.682	4.0	8.0	3.3	1070
14	0	0	1.682	4.0	8.0	6.7	1640
15	0	0	0	4.0	8.0	5.0	844
16	0	0	0	4.0	8.0	5.0	780
17	0	0	0	4.0	8.0	5.0	1040
18	0	0	0	4.0	8.0	5.0	980
19	0	0	0	4.0	8.0	5.0	910
20	0	0	0	4.0	8.0	5.0	912

The resulting empirical equation in terms of coded factors is

$$\begin{aligned} Y = {} & 908.8 + 426.5X_1 + 1.8X_2 + 152.8X_3 \\ & + 37.8X_1X_2 + 133.0X_1X_3 + 137.0X_2X_3 \\ & + 65.6X_1^2 + 228.2X_2^2 + 171.7X_3^2 \end{aligned} \quad (2)$$

The automated analysis of variance (ANOVA), summarized in Table 2, confirms the statistical significance of the model (*F*-value = 37.97, $p < 0.0001$). The lack-of-fit term was non-significant ($p = 0.2579$), thus validating the adequacy of the quadratic model in terms of representing the experimental data within the studied domain.

Table 2. ANOVA results generated by the Python framework.

Source	Sum of Squares	df	Mean Square	*F*-Value	*p*-Value
Model	4,193,415.07	9	465,935.01	37.97	<0.0001
X_1 (G/NCS)	2,484,446.62	1	2,484,446.62	202.46	<0.0001
X_2 (Time)	45.69	1	45.69	0.00	0.9525
X_3 (S/Ni)	318,817.16	1	318,817.16	25.98	0.0005
X_1X_3	141,512.00	1	141,512.00	11.53	0.0068
X_2X_3	150,152.00	1	150,152.00	12.24	0.0057
X_2^2	751,025.10	1	751,025.10	61.20	<0.0001
Lack of Fit	79,659.13	5	15,931.83	1.85	0.2579
Pure Error	43,054.00	5	8610.80	-	-

3.2. Variable Contributions and Pareto Analysis

The Pareto chart (Figure 3) illustrates the standardized effects of the variables. The linear term of the graphene/NCS ratio (X_1) is the most influential factor, accounting for 57.19% of the total variance, followed by the quadratic effect of time (X_2^2, 17.29%). Notably, significant interaction effects were observed between G/NCS and S/Ni (X_1X_3) and between time and S/Ni (X_2X_3), indicating synergistic mechanisms in the material synthesis.

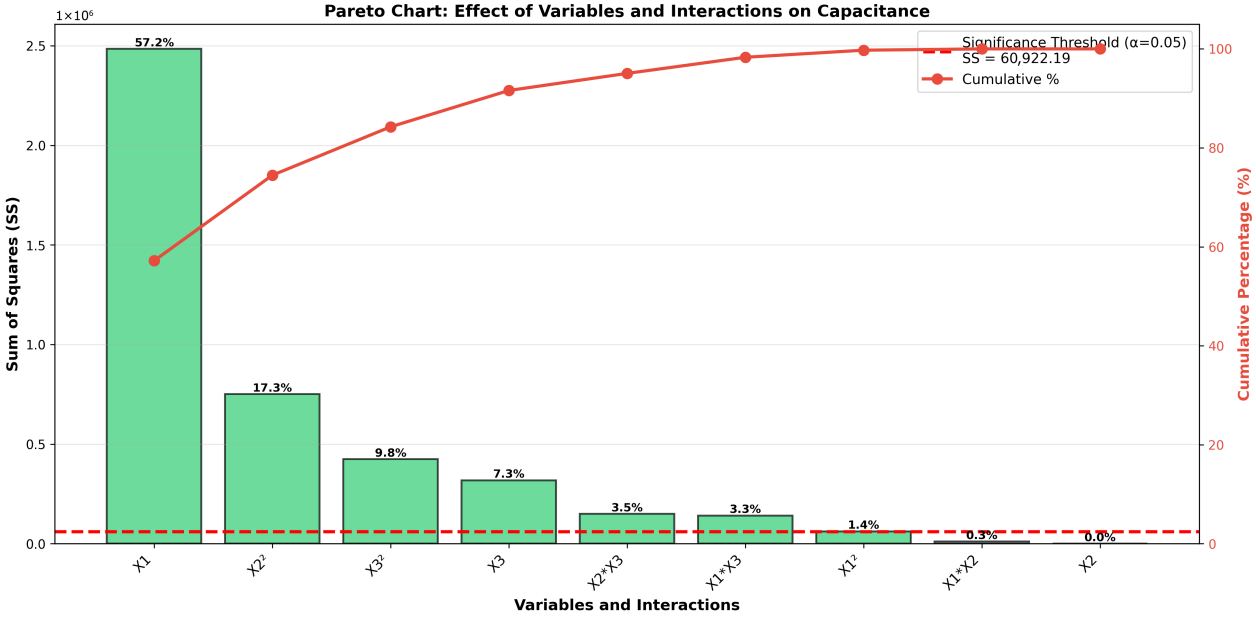


Figure 3. Pareto chart of standardized effects showing the significance of linear, quadratic, and interaction terms ($\alpha = 0.05$).

3.3. Diagnostic and Surface Analysis

A more detailed model diagnosis was performed to supplement standard fitting checks. The residual analysis (Figure 4) confirmed the normality of the error distribution (Shapiro–Wilk $p = 0.8531$). To assess the independence assumption, a plot of residuals versus run order was automatically generated, and the Durbin–Watson statistic was calculated, yielding a value of 1.8288. This value is close to the ideal value, 2.0, indicating there is no significant temporal autocorrelation and confirming that the experimental trials were independent.

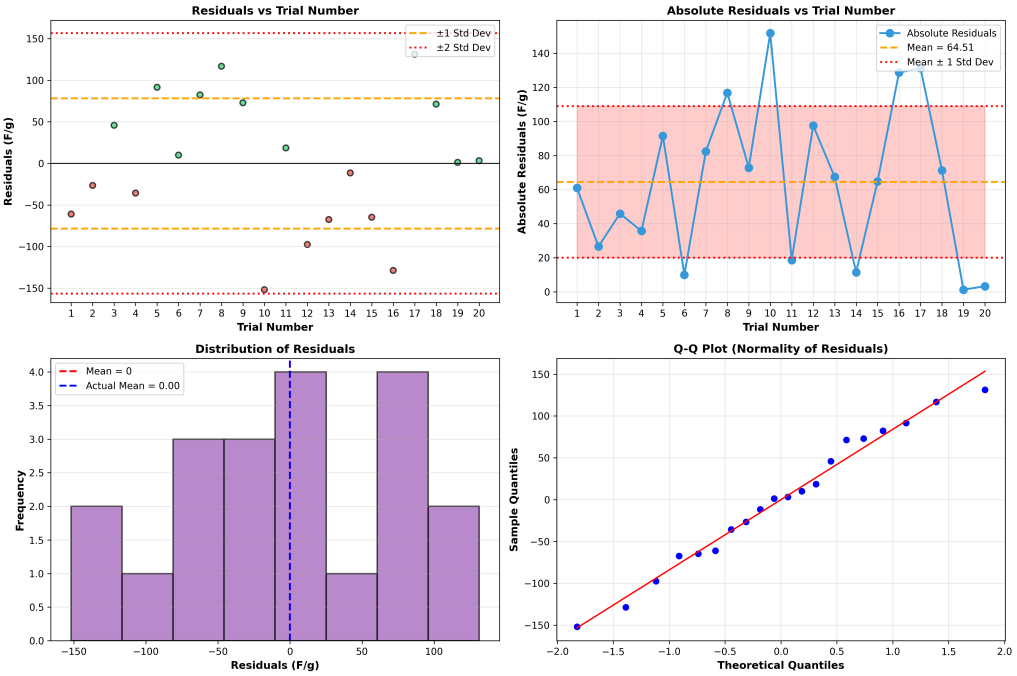


Figure 4. Residual analysis plots: (**left**) normal probability plot, and (**right**) residuals vs. predicted values.

The 3D response surface plots (Figure 5) visualize the interaction effects. The curvature observed in the surfaces associated with X_2 and X_3 reflects the significant quadratic terms, indicating a distinct optimal region within the experimental domain rather than at the boundaries.

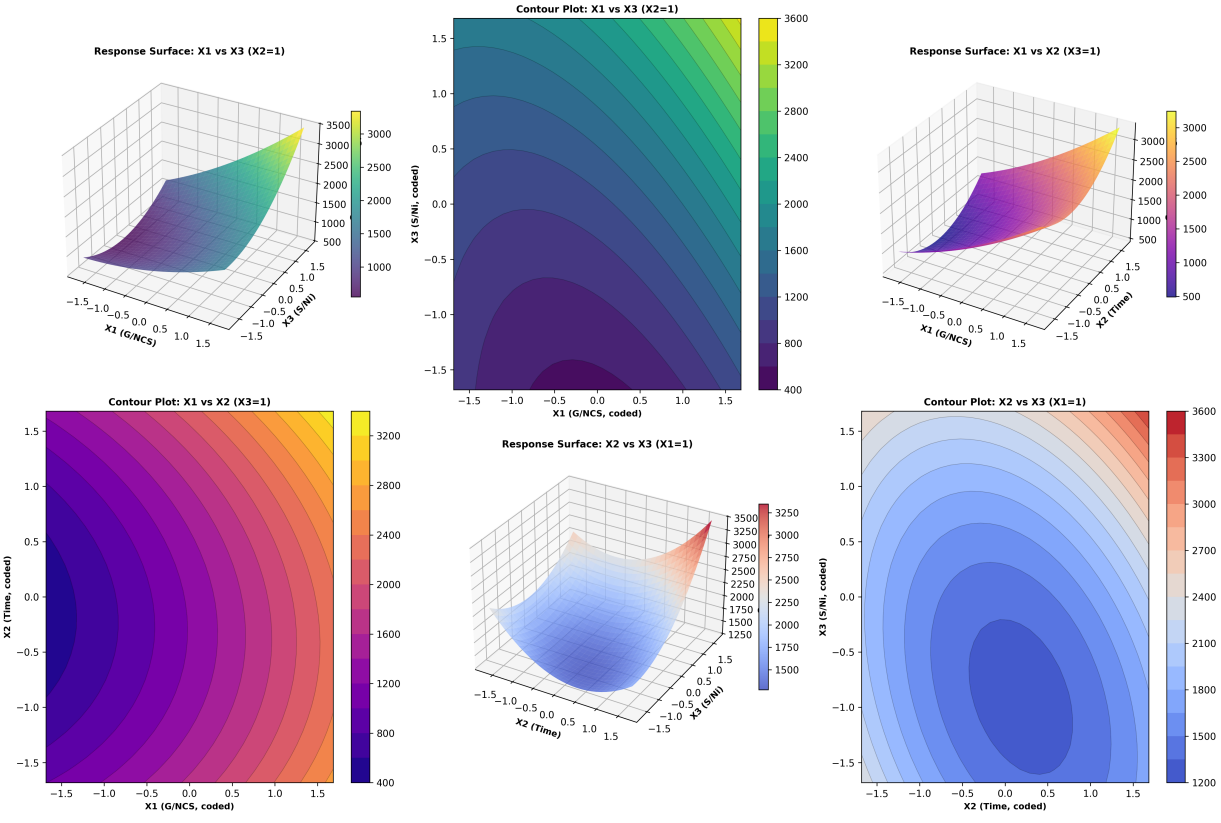


Figure 5. 3D response surface and 2D contour plots showing the interaction between synthesis variables with respect to specific capacitance.

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3.4. Optimization and Validation

The computational optimization, executed via the Differential Evolution metaheuristic algorithm constrained to the factorial region $[-1, 1]$, identified the following optimal conditions:

- G/NCS Ratio (X_1)—1.0 (coded) $\rightarrow$ 6.0%;
- Hydrothermal Time (X_2)—1.0 (coded) $\rightarrow$ 10.0 h;
- S/Ni Ratio (X_3)—1.0 (coded) $\rightarrow$ 6.0.

Under these conditions, the model predicts a maximum specific capacitance of 2263.19 F/g.

4. Discussion

The results obtained with our automated Python framework are in agreement with the original study by Hong et al. [1]. The predicted optimal capacitance of 2263.19 F/g deviates from the value reported in the reference article (2317 F/g) by only 2.32%. The implementation of a global optimizer (Differential Evolution) indicates that this method can be scaled efficiently to high-dimensional problems while mitigating the risk of local optima. Table 3 highlights the differences and improvements offered by the proposed methodology in comparison to traditional procedures.

Table 3. Differences and improvements offered by the Python-based framework in comparison to traditional methods.

Feature	Traditional Methods [1,2]	Proposed Framework
Analysis Environment	Commercial (Design-Expert, Minitab, v7.10.6)	Open-source Python ecosystem
Optimization Algorithms	Gradient/Response Desirability	Differential Evolution (Global Search)
Model Diagnostics	Standard	Comprehensive (Durbin–Watson, Normality)
Scalability	Computationally restricted	Efficient for high-dimensional setups
Reproducibility	Black-box methods	Fully transparent, shareable code

The dominance of the G/NCS ratio (X_1) highlights the critical role of graphene in enhancing the conductivity and surface area of the composite. The significant interactions (X_1X_3 and X_2X_3) suggest that the sulfur concentration (X_3) modulates how effectively the graphene integrates with the $NiCo_2S_4$ matrix.

5. Conclusions

We developed an open-source Python framework for automated Response Surface Methodology analysis. Applied to $NiCo_2S_4$–graphene supercapattery optimization, the framework identified optimal synthesis conditions, namely, a G/NCS ratio of 6.0%, a hydrothermal time of 10.0 h, and a S/Ni ratio of 6.0, predicting a specific capacitance of 2263.19 F/g—a 2.32% deviation from the value in the reference study (2317 F/g). Compared to traditional commercial software approaches, the framework offers open-source transparency, global optimization capability via Differential Evolution, and comprehensive diagnostics, including run-order independence testing.

Author Contributions: Conceptualization, T.F.d.O.; methodology, T.F.d.O.; software, T.F.d.O.; validation, T.F.d.O.; formal analysis, T.F.d.O.; writing—original draft preparation, T.F.d.O.; writing—review and editing, T.F.d.O.; supervision, S.M.P.M. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The Python code used in this study is available at https://github.com/thiagoferrobr/rsm (accessed on 7 September 2025).

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

RSM	Response Surface Methodology
CCD	Central Composite Design
NCS	Nickel–Cobalt Sulfide ($NiCo_2S_4$)
ANOVA	Analysis of Variance
MLR	Multiple Linear Regression
OLS	Ordinary Least Squares
DE	Differential Evolution

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