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Cracking the Code to Electrode-Specific Degradation: Insights from Data-Driven Approaches in ULPING Fabricated Pseudocapacitor

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Abstract **-** To advance research in supercapacitors, it is crucial to develop a cost-effective manufacturing process for pseudocapacitor electrodes that incorporates binder-free and green synthesis methods, along with a single-step fabrication approach. The proposed method, Ultra-Short Laser Pulses for In Situ Nanostructure Generation (ULPING), aims to produce efficient and sustainable pseudocapacitor electrodes on transition metal (Titanium-Ti) without the use of binders or carbon. The research paper focuses on investigating the electrochemical performance of laser-fabricated pseudocapacitor electrodes. The study utilizes the Random Forest (RF) machine learning (ML) technique to establish a theoretical connection between laser parameters and the electrochemical behavior of the pseudocapacitors. The findings highlight the potential of ULPING and ML algorithms in advancing the development of optimal electrodes for pseudocapacitors.

Keywords**:** Pseudocapacitor; binder-free; nanostructure generation; ultra-short laser pulses; data-driven; machine learning; random forest

1. Introduction

Renewable energy sources play a vital role in mitigating climate change, yet efficient storage of their intermittent and location-dependent energy remains a significant challenge [1]. The development of effective energy storage devices (ESDs) is crucial, encompassing both direct storage of renewable energy in rechargeable batteries and supercapacitors, as well as conversion into clean fuels through electrolyzers [2]. Supercapacitors, known for their high-power density and versatile applications, have garnered attention[3]. However, carbon-based supercapacitors suffer from limitations in capacitance and conductivity, prompting the exploration of electrode materials incorporating transition metals (TMs). Conventional synthesis methods for these materials are time-consuming and lack controllability. In response, a novel technique termed ultra-short laser pulses for in-situ nanostructure generation (ULPING) has emerged [4], [5]. ULPING offers distinct advantages over traditional synthesis methods, including environmental friendliness and digital control over key parameters. Recent studies employing ULPING have successfully fabricated improved electrode materials for pseudocapacitors, demonstrating their uniqueness and efficacy [6], [7]. Nevertheless, further advancements are necessary to optimize the interplay between laser parameters, material properties, and electrochemical behavior. Data-driven approaches, particularly machine learning (ML), hold promise for exploring this correlation and optimizing laser parameter selection for efficient electrode production [7]. Hence, ULPING holds transformative potential within the pseudocapacitor industry, warranting continued research efforts in this domain.

2. Methods

During the experimental phase, we generated oxide layers (TiO) on bare Ti sheets using the direct ULPING approach (see Figure 1A). This study employed a two-electrode configuration using a coin cell setup[7]. The electrodes were fabricated using laser treatment, and specific laser fabrication parameters such as power, frequency, pulse duration, and scan speed were recorded (see Table 1). The mix-and-match testing matrix was designed to test each electrode individually against itself and other electrodes, generating a comprehensive dataset for analysis. Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) tests were conducted on all coin cell configurations to evaluate their electrochemical performance. Microscopy analysis, including scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX), provided insights into electrode morphology, oxidation percentage, Ti/oxidation ratio, and porosity (see Figures 1B and 1C). In the computational phase, we utilized machine learning techniques to investigate the correlation between fabrication parameters and performance measures of pseudocapacitors. We conducted a comprehensive empirical analysis employing a widely used supervised learning algorithm in the energy domain: random forest (RF). The purpose of this analysis was to assess their computational efficiency, accuracy, and suitability for predicting the electrochemical performance of pseudocapacitors. Our findings highlight the promising potential of utilizing ULPING to produce nanostructures on transition metals (TMs) for application in pseudocapacitor electrodes[7].

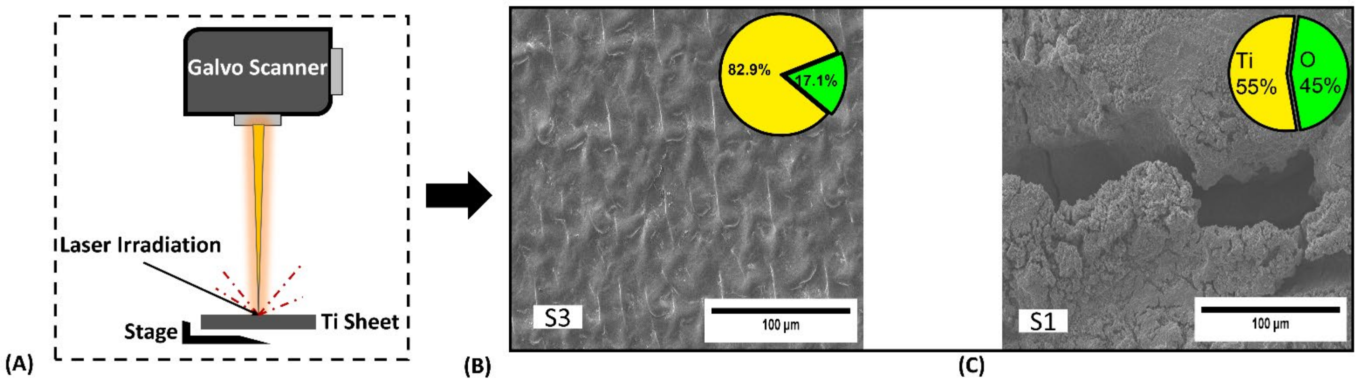

Figure 1. (A) Laser irradiation via the ULPING method. (B and C) Microscopy analysis including SEM and EDX of two samples.

Table 1. Laser parameters for different samples.

Parameters	Type	Range/Style
Power	Variable	5-20 W
Frequency	Variable	30-1200 kHz
Pulse Duration	Variable	150 ps-5ns
Scan Speed	Variable	5-500 mm/s
Pitch	Constant	Arrow sequence

3. Results and Discussion

The analysis of the dataset revealed significant correlations between laser fabrication parameters and electrochemical performance. Microscopy analysis provided insights into electrode morphology and structure, where oxidation percentage, Ti/oxidation ratio, and porosity influenced electrochemical behavior [7]. For instance, microscopy analysis of sample S3 with a scan speed of 60 mm/s showed minor modification, while a lower scan speed of 40 mm/s resulted in extensive surface oxidation and the growth of a self-standing 3D nanostructured oxide layer. The degree of oxidation during laser irradiation, as shown in the EDX results, increased with slower scan speeds, leading to a higher percentage of oxygen detected. Electrochemical analysis validated these findings, demonstrating improved energy storage capabilities with increased specific areal capacitance. S1 with a scan speed of 40 mm/s exhibited the best enhancement in super-capacitive performance, as indicated by a rectangular-shaped CV curve and maximum rechargeable current density (see Figure 2A). Discharge time was influenced by the stable potential window, with wider windows resulting in longer discharge times. S1 depleted stored charges in 8.18 seconds, while S3 depleted in 1.4 seconds (see Figure 2B). The improved specific surface area contributed to S1's excellent performance, as the slower scan speed allowed for a larger area to be irradiated per second compared to S3. EIS analysis further supported these observations, with S1 exhibiting the lowest electrode resistivity of 2678 Ohm.cm^2, indicating superior interfacial charge storage (see Figure 3A).

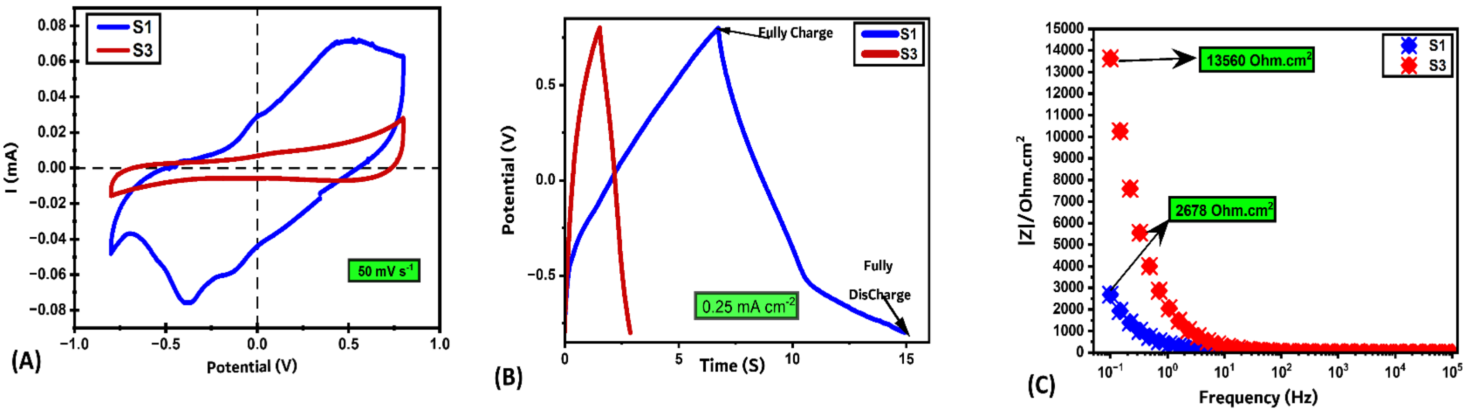

Figure 2. (A) CV profile of two selected samples at 50 mVs^{-1}. (B) GCD curves of S1 and S3. (C) Absolute impedance vs frequency curve proving least electrode resistance for S1.

In addition, we found the computational phase results to be intriguing as they provided a theoretical connection between the fabricated electrodes and their electrochemical performance through the use of machine learning (ML) algorithms. To predict the electrochemical behavior of the fabricated pseudocapacitor electrodes, an ML algorithm was employed: random forest (RF) [7]. Here, we present the results obtained from the RF algorithm. The trained RF model was evaluated using a test dataset, which was split into 80% for training and 20% for testing. Figure 3 illustrates the parity plots of the test sets for the RF algorithm trained on the dataset. In Figure 3A, the predicted values of specific capacitance are plotted against the actual values for the RF model. The RF model achieved a root mean square error (RMSE) score as low as 0.1107 and a coefficient of determination (R2) score as high as 0.8338, indicating the effectiveness of the bootstrap approach in learning the non-linear electrochemical behavior of pseudocapacitors [7]. Figure 3B presents the predicted values of |Z| (impedance) plotted against the actual values for the RF model. Our aim was to provide new insights into the modeling and prediction of the electrochemical behavior performance of fabricated pseudocapacitors. In this study, the RF model was employed to simulate the electrochemical behavior, including impedance and specific capacitance. We have confidence in the RF model's ability to reasonably predict the electrochemical behavior performance metrics, as it ranked first for predicting |Z| values and second for specific capacitance.

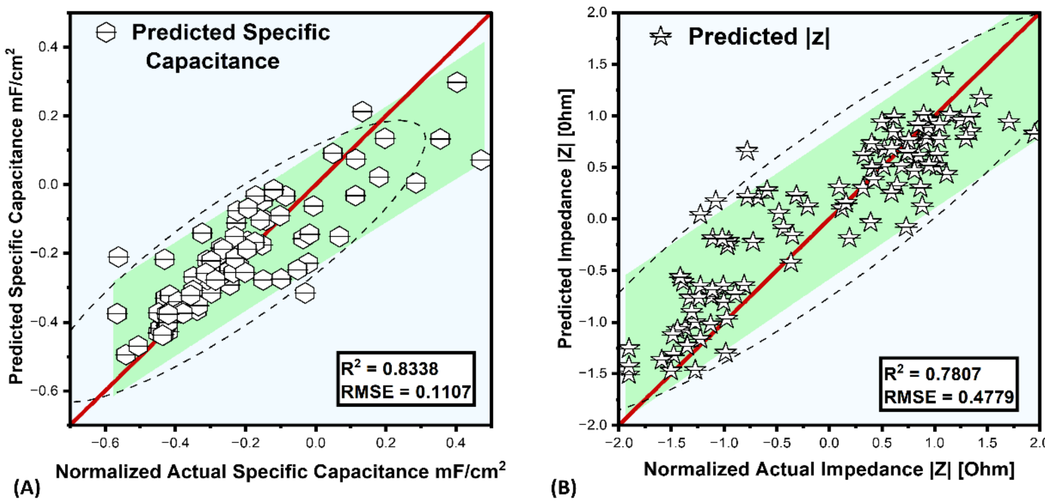

Figure 3. (A and B) Comparison between experimental values for specific areal capacitance and impedance |Z| values and predictions made using the test set with random forest algorithm [7].

4. Conclusion

In conclusion, this research investigated the electrochemical performance of laser-fabricated pseudocapacitor electrodes, emphasizing the influence of laser fabrication parameters on electrode properties and their impact on electrochemical behavior. The generated dataset and testing matrix offer valuable insights for further analysis and optimization of laser fabrication processes. Future studies can focus on refining laser parameters and exploring additional optimization techniques to enhance pseudocapacitor performance. Additionally, the study highlights the potential of machine learning algorithms in predicting electrochemical behavior, aiding in the development of optimized electrodes. The results of this research hold promise for the cost-effective and environmentally friendly production of pseudocapacitor electrodes.

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